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August 1950 Pages 397–464

HOME ECONOMICS

The Journal *of the* SOCIETY OF DYERS AND COLOURISTS

Volume 66 Number 8

CONTENTS

PROCEEDINGS OF THE SOCIETY—

CONTINUOUS PIECE GOODS DYEING WITH VAT DYES INCLUDING THE USE OF MOLTEN METAL (*G. L. Boardman*) 397

CONTRIBUTIONS OF CHEMISTRY AND ENGINEERING TO THE PROBLEMS OF CONTINUOUS DYEING (*R. G. Fargher*) 405

RECENT TRENDS IN THE SEARCH FOR NEW AZO DYES III—DIRECT DYES FOR COTTON (*A. H. Knight*) 410

THE APPLICATION OF LOGWOOD TO WOOL (*C. L. Bird and O. Newsome*) 423

COMMUNICATION—

THE DYEING PROPERTIES OF CHLORINATED WOOL I—QUALITATIVE EXPERIMENTS USING WOOL CHLORINATED AT VARIOUS pH VALUES (*C. B. Stevens, C. S. Whewell, and R. K. Bradley*) 435

CORRESPONDENCE 438

NOTES 439

NEW BOOKS AND PUBLICATIONS 440

REPORTS ON GERMAN INDUSTRY 441

ABSTRACTS 444

THE SOCIETY OF DYERS AND COLOURISTS 32-34 PICCADILLY BRADFORD YORKS

THE JOURNAL
OF THE
Society of Dyers and Colourists

Volume 66—Number 8 AUGUST 1950 *Issued Monthly*

Proceedings of the Society

MANCHESTER SECTION

Meeting held at the Bull and Royal Hotel, Preston, on 15th March 1950,
Mr. R. J. HANNAY in the chair

Continuous Piece Goods Dyeing with Vat Dyes including the Use of Molten Metal

G. L. BOARDMAN

The Development of Continuous Dyeing

INTRODUCTION

The main purpose of this paper is to discuss a new dyeing technique, but before doing this it is essential to outline the background to continuous dyeing. We should know something of the earlier methods, as well as the known modern methods, which have been mainly developed in the United States, in the first place to deal with the large output required by the armed forces. We shall therefore begin very briefly with three methods, which should not strictly be included, viz. the jig, the winch, and the warp dyeing machine.

JIG DYEING

In jig dyeing the cloth is prepared in suitable lots, usually up to 200 lb., and dyed by passing in open width from one roller, through the dye liquor, on to the other roller, repeating several times. The liquor : cloth ratio is usually about 5 : 1, the dye being added in two portions at the beginning of the first and second ends in order to minimise *tailing*, the dyeing of one end darker than the other. The cloth is run four to ten times through the dye liquor in the first instance, and further ends are usually necessary to obtain the correct shade. Oxidation and soaping follow on the same jig. It is usual for one man to operate two jigs, running them together, and the average production per man is 3–6 yards per minute.

WINCH DYEING

Winches are made in a variety of sizes, but it is common for them to have a capacity of 200–300 lb. of cloth; the liquor : cloth ratio is high, of the order of 30–40 : 1. The cloth is immersed in the liquor and turned gently by passing over revolving cylindrical or elliptical winches above the surface of the liquor. Usually the ends of each piece are sewn together, and several pieces are run side by side in the form of endless ropes. Winches are designed principally for dyeing certain types of materials which are not dyed satisfactorily on the jig, such as knitted fabrics, rayons, and delicate fabrics. Output is less than that for jigs.

WARP DYEING

Although this paper is particularly concerned with the dyeing of piece goods, the dyeing of warps is included because it has much in common with a method to be discussed later. It is usual, although other methods have been introduced comparatively recently, to dye warps in rope form, by passing through a dye box fitted with rollers top and bottom and then squeezing with a pair of nip rollers. It is common practice to dye two, four, six, or sometimes eight warps together, running side by side, the length being up to 700 or 1000 yards. Batches of up to 400 or 500 lb. are dyed, and the machine speed is about 25 yards per minute.

Here, again, it is the practice to give four or more runs through the dye liquor, the dye being added either at the beginning of the first and second runs, or a portion at the commencement with continuous feeding. The capacity of the dyebath may be up to 300 gallons, and it is common to use two or more such dyebaths together, so that the yarn passes through one, is squeezed, and then passes through the next, giving longer immersion in the dye liquor for each run.

Warps have been dyed in continuous form by modifying this method, a machine with three or four such boxes being used, and the speed reduced to give the necessary immersion time. Generally speaking, this method is confined to black or single-colour shades, because of the very great difficulties encountered in maintaining the dyebath at uniform composition.

PIECE GOODS DYEING

To return to piece goods, the earliest attempts at improvement are very simple and follow closely along the lines used for dyeing warps; that is, trying to achieve in one run through the dye liquor what normally requires several runs, simply by lengthening the passage of cloth through the liquor. The

time of immersion in the liquor varies with depth of shade and different dyes, usually being about 3 min., but with certain dyes such as Caledon Blue R it can be as little as 30 sec. The machine again consists of an iron tank holding 200–300 gallons with a series of rollers top and bottom allowing the cloth to pass in open width; a pair of rollers remove the liquor after dyeing. Several such tanks can be used in series, both as additional dyebaths to increase the time of dyeing, thus giving fuller shades, and also for washing and soaping, etc. In other words, the machine is very similar to the normal open-width soaping range and similar to the warp-dyeing range. The dye feed liquor is gravity-fed from a tank placed above the machine.

The most serious objection to this type of dyeing (including the continuous warp method) is that the dye has to be replaced as it is removed from the bath, necessitating the use of a constant feed. Determination of the composition of the dye feed liquor necessary to maintain a dyebath of constant composition is practically impossible, even with a single dye. It will readily be seen how variations of temperature, chemicals, or cloths will alter the rate of dyeing. With compound shades the difficulties are increased, because as most dyes have different affinities they require replacing at different rates. Variation of tone as well as of depth of shade occurs, and feed liquor calculation becomes almost guesswork.

It can readily be seen that evenness and uniformity of dyeing are not characteristic of this method. Shade matching is by no means easy, the quality of work is not very good, only certain dyes can be used in combination, and the speed and output are very limited. In fact the piece dyeing method has only a very limited application, and has never achieved great popularity.

LEUCO PADDING

A later development which is really a modification of the previous method is the leuco padding method. It consists in applying the dye in the reduced or leuco form in a comparatively small dyebath of 2–3 gallons capacity, and squeezing by passing through a padding mangle. Oxidation, washing, soaping, etc. follow in the usual type of open-width soaper.

The method has many very serious limitations, which confine its use to the dyeing of pale shades on cloth which is easily penetrated. Levelness and fastness are only moderate, colour value is low, and only dyes with low affinity are suitable. The shade varies with the speed of the machine, and colour matching is difficult.

Although the disadvantages are so great as to make it practically useless for really good work, we should consider it a little more closely. In the previous method the dyebath and feed liquor were of different strength and composition. In order to simplify this the dyebath has been reduced from 200–300 to 3 gallons, the aim being to achieve an equilibrium reasonably quickly and use the same liquor for both dyebath and feed. As the cloth is dyed during its passage through the dyebath, it takes up about 70–80% of its own weight of dye liquor. There is a weakening of the strength of dye liquor due to absorption of the dye by the cloth, and addition of feed liquor of the same composition therefore will not make up the strength to the original, but an equilibrium will ultimately be reached. The smaller the dyebath the sooner the equilibrium is reached, but also the smaller the dyebath the smaller the duration of immersion, resulting in poor penetration and fixation. It will be seen, therefore, that a compromise must be made, and a dyebath of approx. 3 gallons is considered to be most suitable.

With a single-colour dyeing, attainment of equilibrium shows itself in a gradual weakening of shade until it is achieved, but with a compound shade of two or more colours a change of tone as well as depth is apparent.

PIGMENT PADDING

The methods discussed up to now have been of general interest rather than of general application, but we come now to the methods which have achieved some considerable success, have been well tried, and are running to-day on a very considerable scale. These have been introduced during the last ten years, and have been made possible by the modern fine vat dye pastes and powders, which in combination with modern dispersing agents are very suitable for pigment padding. The object of this procedure is to introduce the dye to the cloth in an inactive form, enabling it to penetrate the material without dyeing taking place on the surface before penetration is achieved. This process is used very largely in this country, where the reduction and dyeing take place subsequently on the jig, but of course this is not continuous processing. It is, however, the basis of the main American continuous dyeing processes.

The modern vat dyes have also made possible rapid reduction at high temperature. The generally recommended procedure for reducing vat dyes is to disperse the dye in water at the correct vatting temperature, which is usually 50–60°C., add the requisite amounts of caustic and hydrosulphite, and allow to stand for 10–15 min. This period of time certainly gives a very safe margin, and it has been found that if the temperature is raised to the region of 95°C. with suitable caustic and hydrosulphite quantities, reduction can be achieved in a few seconds. This is the second factor upon which American continuous dyeing practice depends.

BOOSTER BOXES

The first of these processes to be introduced consists in developing or fixing pigment-padded cloth in *booster boxes*, charged with alkali and reducing agent, at a high temperature.

The dry cloth is passed first into the padder, where the vat dye is applied as a fine aqueous dispersion, the excess being squeezed out to about 70% on the weight of the cloth, which is then passed to a continuous hot-flue drier, where the water is removed, leaving the dye dispersed throughout the cloth but not fixed. Incidentally, the strength of the dye suspension is easily maintained, since the dye is mechanically attached to the cloth. The hot flue is more suitable for drying pigment-padded cloth than steam cylinders, which

cause migration of dye to the surface and subsequent poor appearance of the finished cloth.

After drying, the cloth passes to a three-bowl padder, where it is impregnated with a cold caustic and hydrosulphite solution containing salt. Bleeding of the colour is minimised by the use of low temperature and salt.

Reduction and fixation are completed in the booster boxes, where the cloth is passed in open width over a series of rollers in a bath containing caustic and hydrosulphite solution at a temperature usually between 75° and 100°c. The booster boxes are of large capacity, holding several hundred gallons, and an immersion time of about 1 min. is required to develop and fix the dye. The cloth is then oxidised, washed, and soaped in the usual open-width soaper range.

Speeds of the order of 100 yards per minute are claimed, although the average running speed is probably nearer 50 yards per minute.

Shade matching is done by running small pieces of the cloth through the machine itself.

Booster baths are used in one form or another in several continuous dyeing methods, so we should at this stage discuss them a little more fully.

When pigment-padded cloth is passed into a caustic and Hydros solution at high temperatures of approx. 100°c., there are two mutually opposing effects— firstly, a very rapid reduction to the leuco compound within the material and rapid dyeing, and secondly, the stripping action of the hot reducing liquor on the dye. These continue until an equilibrium is reached. Thus the effect of the high-temperature reducing liquor is to give rapid dyeing but at the same time to increase the stripping action.

Thus a large bath is required to give the immersion time necessary for high speeds, whilst in order to minimise the stripping action or to reach equilibrium quickly a small bath is necessary. The effect of the large booster bath may be minimised by additions of salt and by adding dye before commencing the run in order to reach equilibrium more quickly, but as the amount required varies with each dye and cloth, etc., this method is not completely satisfactory. Furthermore, a considerable amount of dye is wasted in large boosters, particularly when using those with lower affinities and when dyeing medium and full shades.

DU PONT PAD–STEAM PROCESS

One of the most successful American continuous dyeing processes is the Du Pont pad–steam process. The cloth, after pigment-padding and drying, passes over a cooling cylinder (to minimise bleeding), into another padding mangle containing caustic and hydrosulphite solution below 40°c. with salt or Rongalite also to minimise bleeding. After removal of excess liquor to about 70% of the weight of the cloth on the mangle, the impregnated cloth passes into a steamer, where it is subjected to an atmosphere of saturated steam at or slightly above 100°c. Exclusion of all air is necessary at this stage, and it has been found that under such conditions reduction and fixation are completed in less than 1 min., and frequently 10 sec. is all that is required. After steaming, the cloth is oxidised and soaped in the usual manner.

This was the method first introduced as a commercial process, and it will be noticed that it is a rearrangement and modification of old processes.

It is now usual to run this as a two-stage process, with the pigment-padding and drying in one stage, and the reduce pad, steam, and finish as the second. Work was carried out to omit the intermediate drying after padding, but results did not appear to be too satisfactory.

It has been found that with certain cloths and dyes, complete fixation throughout the cloth is not achieved with steaming alone, and liquid boosters are now arranged in the bottom of the steamer, so that the cloth passes through the steam and into the liquid boosters on several occasions.

The volume of these boosters is much less than in the earlier methods, but is still considerable. Here, again, dye is added to the booster baths before the commencement of the run in order to attain equilibrium quickly.

High speeds of 100 yards per minute are claimed with this process, but it appears to be more usual to run at a speed of the order of 60 yards per minute.

WILLIAMS UNIT

The Williams process is also a very successful American method, and also uses the pigment-padder and drier as the first stage of its treatment. Development takes place in either one or two of the Williams units, which are the usual tanks with rollers top and bottom, except that much of the space between the cloth on its passage up and down is occupied by baffles and heaters.

This means that in effect the volume is reduced to about 80 gallons, and the cloth passes through very narrow compartments, taking along a considerable amount of the reducing liquor with it. This liquor overflows from the last compartment back to the first, and its strength is maintained by constant controlled additions of caustic and hydrosulphite. The temperature is maintained near 100°c. by means of heated baffles, and at this high temperature very rapid reduction and fixation occur.

Although the volume has been very considerably cut down, it is still necessary to add dye at the start of the run to speed up the attainment of equilibrium.

The inventor claims that the relative movements of cloth and dye liquor lead to improved penetration of the dye.

Speeds of the order of 100 yards per minute are again claimed, but the normal running speed appears to be in the region of 60 yards per minute. Oxidising and soaping, etc. follow along the usual lines, although it is interesting to note that the Williams units may also be used for washing and soaping.

REVIEW OF AMERICAN PROCESSES

It is not intended to discuss the American Multilap process, because it has been designed specifically for handling delicate fabrics, and is

very similar in principle to the pad–steam process of Du Pont.

Of the processes that have been described, the Du Pont pad–steam and the Williams unit have certainly been the most successful; opinion varies somewhat on the merits of each, and both are being widely used in the United States.

In both cases high speeds can be maintained for long periods, and they are best suited for long runs of 10,000 yards and over. The speed can be varied within certain limits without affecting shade.

It is claimed that all dyes can be successfully used, although the vat blues present certain problems.

Shade matching is done in both cases by running pieces of cloth through the machine itself.

After completing a dyeing, the booster boxes are drained, cleaned out, and replenished for the next dyeing. The time required for this operation depends, of course, on the extent of change: sometimes it is possible to use the same booster bath for more than one lot providing the shades are very similar, but generally the change has to be made, and may take 3–4 hr.

DISADVANTAGES OF DYEING VAT DYES ON THE JIG

A continuous dyeing process should overcome the difficulties encountered in dyeing vat dyes on the jig, which may be listed as—

(1) Atmospheric oxidation effects— dark selvedges, mottling, etc.

(2) Stains due to sewing repeats, design repeats, etc., due to the fact that most of the dye absorption occurs on the batch roller, and sewings and thinner parts of the fabric hold more liquor.

(3) Stained batch ends, due to cold rollers and premature oxidation.

(4) The difficulty of getting perfect matchings from batch to batch in a large order. This is quite understandable when it is realised what considerable differences may be caused by comparatively small variations of liquor ratio, small differences of temperature, and variations in quantities of e.g. retarding agents. Even though the dye may be the same in each case, quite noticeable differences can occur from these causes.

(5) The difficulty of predetermining results, i.e. the almost impossible task of matching shades in the laboratory and transferring to the jig. Even though the bulk may come out fairly near to the laboratory dyeing, it cannot be relied upon to be an exact match; patterns have to be taken, and more often than not additions made.

(6) Restriction of choice of dye combinations. It is very difficult and in some cases practically impossible to dye certain dye combinations satisfactorily. For example, a mixture of a hot-dyeing dye and a cold-dyeing dye must be dyed at a compromise temperature, and consequently one or the other or both are not dyed under the optimum conditions.

(7) When dyeing cotton–viscose mixtures on the jig there is the difference of affinity of these two fibres for the dyes to be reckoned with, as a result of which the viscose tends to be dyed much darker than the cotton. This can be overcome to some extent by various modifications, but it is not always an easy matter. The pigment-padding process does very greatly minimise this trouble.

DESIDERATA OF CONTINUOUS DYEING PROCESS

Any really successful continuous dyeing process must eliminate, or at least greatly minimise, these difficulties, but at the same time it must also have the following characteristics—

(*a*) Economy of processing in chemicals, steam, and labour, which must compare favourably with jig-dyed goods. Economy in chemicals is ensured only by obtaining maximum dye fixation during dyeing and minimum dye loss. Thus obviously the aim must be to have small dyebaths or booster baths and a low liquor : goods ratio, so that dye and chemicals discarded after dyeing are small. In order to obtain economy in labour it must be a fairly simple process that can be run with a small staff.

(*b*) Ease of changing from one shade to another. When a unit can produce at speeds of 100–120 yards per minute, it is obvious that stoppages must be cut down to a minimum, or a large amount of production is lost and the average speed is very considerably lowered. With a continuous dyeing machine the main cause of stoppage is changing shade, so that, particularly when considering small yardages, the time taken to change shade must be cut down to a minimum.

(*c*) Cleaning down must be simple, and all shade matching must be done previously— it must be possible to transfer accurately laboratory matchings to the bulk machine without running trial pieces through the machine. Incidentally, shade matching has always been a serious problem with continuous dyeing.

(*d*) It must be capable of handling a large output of cloth at economically high speeds, but at the same time it must be possible to dye small lots also economically. This is, perhaps, a point more for consideration in this country than in America, where the work is somewhat different. It is seldom that we over here get runs much larger than 5000 yards, except for print ground shades, and more often than not they are in the region of 1000 yards. Not very long ago a figure of 8000–10,000 yards was given as an economic minimum for American continuous processing. The main factors influencing the economical minimum yardage are the time and ease of changing from one shade to another, the speed at which equilibrium is reached, and the quantities of unused dye and chemicals left in the baths at the end of the dyeing.

(*e*) The quality of the work must be at least as good as, and preferably better than, that dyed by any other method, as regards good shade matching, uniformity, penetration, and levelness of shade throughout.

(*f*) It must be possible to accommodate and dye satisfactorily widely varying types of cloth any colour from very pale to very dark shades.

(*g*) The speed must not influence the shade produced. Obviously it is inconvenient to have to alter dye concentrations and feeds if the speed is increased.

(*h*) The feed liquor should have the same composition as the dyebath irrespective of the dyes used, and any equilibrium should be reached almost immediately. This problem is not solved by adding dye to the boosters to speed up the equilibrium.

(*i*) It must be possible to dye the full range of vat dyes, either singly or in combination with each other.

(*j*) Any dye liquor or booster liquor must be held at high temperatures for only a short time, because firstly the hydrosulphite is not very stable at high temperatures; constant additions may be made, but this requires careful control to maintain uniformity. Secondly, many vat dyes are not stable at high temperatures in the reduced state; those of the Blue RC type rapidly lose fastness to chlorine, and the dyeing properties are eventually destroyed.

This list of requirements may appear to be rather formidable, but it must be borne in mind when considering continuous dyeing. Claims of extremely high speeds must not cause us to overlook other very important points. In this country these very high speeds, although very desirable, are by no means the most important feature.

The Standfast Molten-metal Machine

Since 1945 a programme of intensive research has been undertaken at Lancaster on vat dyeing by continuous methods. The original idea was simply to find a method of dyeing piece goods more easily, more efficiently, and of better quality than by the usual methods. It soon became apparent that the conditions likely to achieve these results were also ideal for continuous processing, and the aim then became to work out a continuous dyeing process with high quality as its greatest asset. The outcome of this work has been the development of a novel method of dyeing, which at the present time has exceeded even the most hopeful and imaginative dreams of those early days.

The principle involved in the process is the use of molten metal as the medium in which fixation of the dye occurs, hence the name. The cloth is simply impregnated with dye liquor and passed through the molten metal, where dyeing is completed*.

The unit consists of two parts, the dyeing machine and the conventional soaping range, but both are run together as a single unit.

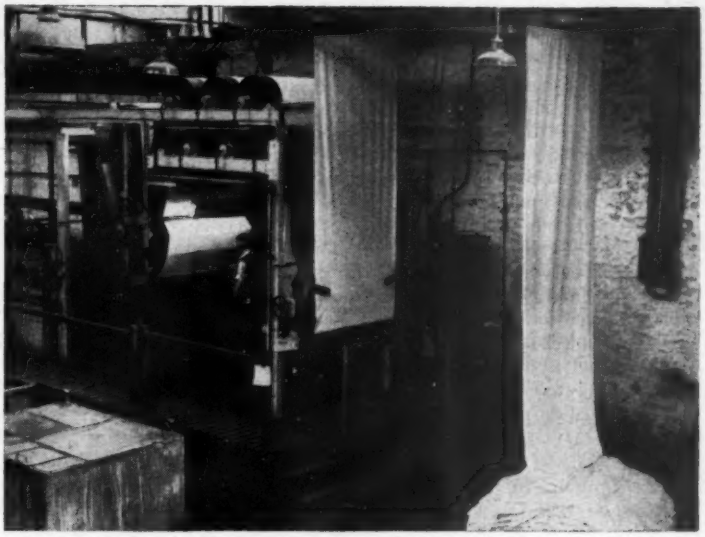

FIG. 1—The Standfast Molten-metal Machine

DESCRIPTION OF MACHINE

The dyeing machine itself (Fig. 1) is extremely simple, consisting of an iron vessel (Fig. 2) filled with molten metal of the fusible alloy type, having a melting point of approx. 70°C. The machine has two legs 5 ft. long, about 1 in. wide and 6 in. apart, joined together at the base, where there is a roller to allow the cloth to pass freely from one to the other. The width of the machine is 5 ft., which gives in fact a large U of metal 5 ft. wide, 5 ft. deep, and 1 in. thick. The cloth is passed in open width down one arm of the U tube and up the other, giving a total passage through the metal of a little over 10 ft. At certain intervals down both legs of the machine

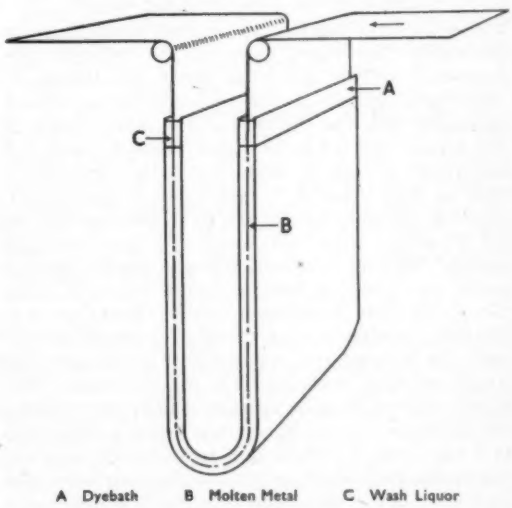

FIG. 2—Diagrammatic Sketch of the Standfast Molten-metal Machine

* Readers may be interested in the following references to the use of fusible metals in textile processing—

Mather and Hepburn, *B.P.* 24,617 (1903).
I.G., *F.P.* 900,758.
BIOS 514 (London: H.M. Stationery Office), p. 62.
—*Editor.*

and on both sides of the cloth steam heating pipes are arranged, so that an even temperature is maintained throughout the molten metal.

At the surface of the metal on the entry side, there is a bottomless stainless-steel dyebath extending the full width of the metal slot, this being 5 ft. long and less than 1 in. wide. The height of the dyebath is such that there is almost 8 in. above the surface of the metal and 2 in. below. When the dyebath is filled, the liquor floats on the surface of the metal, which acts as the bottom of the dyebath. The reason for having the dyebath sides extending below the metal surface is that the molten alloy used has a density of about 9, so that an 8-in. column of dye liquor depresses the surface of the metal about 1 in.

During dyeing, the cloth in continuous length is passed through the dye liquor directly into the molten metal. In the dyebath it becomes thoroughly saturated with dye liquor, and all excess is squeezed out by the pressure of the metal. During its passage through the molten metal, which is maintained at 95–105°c., dyeing takes place, and on leaving the machine the exhausted dye liquor is removed in another bath very similar to the dyebath but this time containing salt solution as wash liquor. The dyeing is now completed, and the cloth passes into an open-width soaper, where it is oxidised, washed, and given a thorough soaping and final successive washings before being nipped and plaited down on waggons for drying.

Thus the process is continuous, with white cloth being fed in at one end and emerging ready for passing over the drying cylinders at the other.

FUNCTIONS OF THE MOLTEN METAL

It will be obvious that the molten metal plays an extremely important part in the process just described, and we should at this point discuss its main functions. In the first place it has a uniform squeezing effect on the cloth. The metal, being in the liquid state, exerts equal pressure from all directions on a point below its surface and, being able to flow readily, it can modify the surface applying pressure to conform to the surface requiring pressure. Thus in the case of a material with greatly differing thicknesses as in certain types of cloth, e.g. a velvet having a thick pile and comparatively thin selvedges or certain fancy weaves, the metal is able to adapt itself to these differences and give a constant proportion of liquor per unit weight of cloth irrespective of the thickness. The metal squeeze gives an expression of approx. 140%, which means that we dye with a liquor : cloth ratio of 1·4 : 1. On the other hand, with liquor squeezed out on the padding mangle the rollers are inflexible, squeezing out a maximum from the thick portions and retaining more on the thin. On development in such cases, particularly in rapid continuous processing, the thin parts are dyed much darker than the thick. On the metal machine a uniform shade is obtained.

The pressure at the base of a 5-ft. column of metal is 20 lb./sq. in.

The second function of the molten metal is complete exclusion of air during dyeing. The dye liquor and cloth on passing into the metal are completely protected from air oxidation, thus removing one source of numerous troubles in dyeing vat dyes. It will be remembered that the trouble of dark selvedges in jig-dyed fabrics is due to this partial premature oxidation of the reduced dye, whilst another similar trouble is caused on the jig by some cloths tending to trap air inside the batch. By preventing contact with air these and many other troubles are removed.

The third function, again a very important one, is that the metal acts as a source of heat in intimate contact with the dye and fabric, giving a rapid transfer of heat. We have a metal temperature of 95–105°c., an extremely short liquor ratio, complete exclusion of air, which would act as an insulator, and the dyeliquor-impregnated cloth immersed in the metal, so that a very rapid transfer of heat takes place throughout the fabric. The combination of these points makes it possible to dye *all* vat dyes at 95°c. This high-temperature dyeing is extremely advantageous, providing conditions are right, because the transfer rate of the leuco dye from the dye liquor to the fibre is greatly increased at such a temperature, particularly when using as we do a very small liquor ratio.

Increased penetration and full fixation and fastness are obtained in a few seconds. Even dyes like Caledon Red BN (ICI), which is normally dyed cold with large additions of salt, dye very successfully at 95°c., and in fact this dye has one of the most rapid transfer rates at such a temperature. All vat dyes, irrespective of which dyeing groups they belong to, dye equally successfully under these conditions.

Another extremely interesting point is that all vat dyes are dyed on the metal using similar quantities of caustic and hydrosulphite, etc., no matter whether they belong to group 1, 2, or 3. Therefore, we can, and do, use any combination of dyes, no matter whether they be normally cold- or hot-dyeing, and in all cases we obtain full colour value. We have experimentally obtained excellent dyeings with mixtures of such dyes as Caledon Blue RC, Red BN, and Yellow G, although we do not make a practice of going to such an extreme.

SPEED

The dye transfer rate is one of the most important factors controlling the speed at which the machine can be run, and whilst it varies slightly with different dyes and depths of shade, it is in all cases only a few seconds. We can therefore dye any vat dye or combination of vat dyes at any depth of shade at speeds upwards of 30 yards per minute, which is the minimum speed at which the machine can run.

The maximum speed that we have achieved is 120 yards per minute, this upper limit being fixed by mechanical considerations; perfectly satisfactory dyeings are obtained at this speed.

Such speeds as these show how rapidly the dye transfer and fixation are completed. The passage through the metal is 10 ft. and through the dyebath 8 in., so that at 30 yards per minute the cloth is immersed for 0·44 sec. in the dyebath and

6·7 sec. in the metal. At 120 yards per minute we have 0·11 sec. in the dyebath and 1·67 sec. in the metal. At the end of these times the dyeing is completed.

In actual practice variation of speed has no effect on either depth of shade or quality of dyeing, providing it gives the time required for fixation in the metal. Thus, if we are running a cloth at 100 yards per minute with complete fixation, we can slow down to 30 yards per minute or vary the speed as often as we like with no influence on the shade.

The above is the broad outline of the process that we have developed, which is now running as a production unit in the factory. Up to the present time over six million yards of cloth have been dyed by this process, and one machine has produced as much as 45,000 yards in one single 11-hr. day.

PROPERTIES OF THE MOLTEN METAL

The original work was carried out on the laboratory scale using mercury as the molten metal. Extremely promising results were obtained, and actually mercury is an ideal metal in many respects, but in view of the health hazards connected with this metal, it was decided to investigate the possibility of an alternative. The metal chosen as being most suitable was an alloy similar to Woods' metal, containing bismuth, cadmium, tin, and lead. It has a melting point of 71°C. and a density of 9; when molten it is very similar in appearance to mercury, but possesses the great advantage of having no health risks. It has, however, the slight disadvantage of a higher melting point, and this means that anything coming in contact with the molten metal during the dyeing must be at a temperature greater than 71°C. Consequently, the dye liquor, the wash liquor, and the cloth must be above that temperature before coming into contact with the molten metal. Actually in practice it has made very little difference, except that the cloth is heated just prior to dyeing, by passing over steam-heated cylinders, and that the dye liquor is at a temperature of 75°C. on entry into the dyebath.

SHADE MATCHING

One of the most important features of this method of dyeing is that all shade matching is carried out beforehand, and transferred accurately to the bulk machine. This is not possible with any other form of dyeing process. Our technique is for an assistant chemist to match the shade as soon as patterns and cloth are available, on a small model of the large machine, with speed adjusted accordingly. He does this by running small pieces of the prepared cloth through his machine: the weight does not matter. The dye liquors are made from standard suspensions and known concentrations of chemicals made up to known volumes. The dyebath holds about 100 c.c., and a pattern is run through the machine in about 15 sec. Of course, there remain the oxidising, soaping, and drying, but it is a fairly quick method. This is an extremely important stage, and care must be taken to have dye suspensions of the correct strength to ensure that the results are reliable. The recipe when completed is given not in the form of percentages, but as concentrations of dye and chemicals in grams per litre.

Some time before the cloth is to be dyed—probably an hour or two—the dye is made up in bulk to this recipe, and as we have several dye tanks the dye can be made up several shades in advance. Just as a precautionary measure against mistakes in weighing, etc., a further sample of this liquor is run through the small machine. After this check has been made, we know that the dyeing can proceed, and without running any trial pieces through the bulk machine we know just what the finished shade will be. This is an enormous advantage, saving a great deal of time, and replacing the usual rule-of-thumb methods by technical control.

DYE LIQUOR

It has already been mentioned that the dye liquor is at 75°C. on entering the dyebath, but sodium hydrosulphite is not very stable, and even in alkaline solution it is fairly quickly decomposed at high temperatures of this order. Furthermore, several vat dyes are not stable in alkaline hydrosulphite solutions above 60°C. for long periods, and with the concentrations of chemicals we use, even at this temperature of 60°C. some degradation of certain dyes is apparent after about 20 min. The dyes principally concerned are the blues of the Blue RC type, although several other vat dyes are adversely affected by prolonged treatment at high temperatures.

In view of these facts we do not store our dye liquors at 75°C. The dye liquor is made up cold to the required volume along with caustic and hydrosulphite in higher concentration than are normally used, also dispersing and wetting agents. It is stored cold until immediately before use, when it is heated very rapidly by passing through an efficient heater on its way to the dyebath.

The hydrosulphite and dyes are reasonably stable for several hours at this low temperature. No attempt is made to obtain reduction at this stage, although a certain amount does occur with some dyes. Reduction and solution are achieved in 5–10 sec. during heating, on passage of the dye liquor to the dyebath and through the molten metal, this being possible with the modern finely dispersed vat dyes.

DYEBATH

The dyebath itself on the Standfast machine is unlike the conventional type of dyebath in many ways, but particularly in its extremely small capacity (it holds slightly more than one gallon) and also in that it is the place where the utmost is done to prevent the cloth from being dyed. What is aimed at is for the cloth to become thoroughly wetted out and saturated with dye liquor. The cloth is heated just prior to entry into the dyebath, and this also ensures that the cloth is completely dry and hence will receive the dye liquor uniformly. On becoming saturated, the cloth passes into the molten metal, and excess dye liquor is squeezed out to an expression of 140%.

When designing a dyebath for this purpose the question of size becomes extremely important. The dyebath, and also for that matter the whole

machine, must be adaptable to all types of cloth and to all speeds. This means that it must be capable of handling dye feeds varying between ½ and 10 gallons per minute, depending upon the speed and weight of the cloth. This obviously is easier to achieve with a large-capacity dyebath. But on the other hand we must cut down to a minimum the amount of dyeing taking place. This would ideally be achieved by applying the liquor to each unit portion of the cloth without allowing it to come in contact with any other, in other words from a dyebath of infinitesimally small capacity. As this is impossible, the dyebath must be designed small enough to ensure as rapid replacement of the whole of the contents as possible.

With a dyebath of one gallon capacity we find that these aims are achieved satisfactorily. The dye level is maintained automatically to within less than ¼ in. with any rate of liquor consumption up to 10 gallons per minute. Furthermore, with this capacity we find that replenishment is sufficiently rapid to eliminate any signs of tailing, which would arise from a large dyebath.

FEED LIQUOR

There is another very important factor governed by dyebath size, viz. feed liquor concentration. In the first attempts at continuous dyeing, a large dyebath necessitated the use of a feed liquor of different composition from that of the original dyebath (p. 398). With the one-gallon bath of the Standfast machine and the relatively high liquor consumption these difficult feed liquors are eliminated, and the same liquor is used for both the original dyebath and the feed liquor.

SHADE CHANGING

At the end of a dyeing, the dye liquor remaining in the system is pumped out, and hot caustic and Hydros solution is pumped through the whole system to clean it. After circulation the cleaning liquor is removed and replaced by the next dye liquor. Dyeing of the second shade commences immediately. The time required to effect a complete change from one shade to another averages 5 min.; in changing to a similar shade it is less, but to change from, say, a heavy green to a pink may take a little longer. As these estimates are taken from the moment that one shade leaves the metal until the next dyeing begins, they compare favourably with earlier methods of dyeing, where 3–4 hr. may be required.

PENETRATION AND AUXILIARY PIGMENT PADDING

With regard to penetration, fabrics dyed on the Standfast machine are superior to similar ones dyed on the jig, because of the nature of the application—the high temperature, the pressure of the molten metal, and the receptive nature of the cloth as it enters the dyebath.

Even so, we sometimes wish to get even better penetration on some tightly woven fabrics, and then we pigment-pad before dyeing. This involves the use of the normal type of padding mangle as discussed with the Du Pont machine and the Williams unit (p. 399), and we always dry after padding. This stage of the process is run as a separate unit, the cloth in continuous length passing through the padder into a hot air drier and when dry on to waggons. Some time later the cloth is run through the metal machine, using the liquor left over from the padding, made up to suitable volume, with caustic and hydrosulphite, etc. added. Development is again extremely rapid and the rate is of the same order as in the normal dyeing methods. The dyeing from this stage proceeds exactly as before. With other methods involving pigment-padding, shade matching is difficult, but in our method it is still a simple matter. A normal matching is first carried out, and the amount of dye is calculated from the recipe, being diluted to the amount required on the padder. As we know how much liquor will be required on the metal machine, the unused dye is diluted to that amount and a check dyeing made.

In actual practice the amount of work that we pigment-pad is only a very small percentage of the total, our main bulk being dyed by the straight dyeing method. This is an enormous advantage, since most cloths do not need to be pigment-padded.

VERSATILITY AND PRODUCTIVITY

The types of cloth that we have dyed on this machine include cotton plains, slubs, brocades, cotton–viscose brocades, all-viscose brocades, spuns as brocades or plains, linen plains, and damasks; also towels, nets, marquisettes, and velvets.

Comparisons of labour requirements are not very easy, particularly between our machine and American Du Pont or Williams units, because the type of work is so dissimilar. The Americans very seldom handle less than 10,000 yards, whilst we handle any length from one piece upwards. But for long runs our requirements are at least one man less than those claimed by the Americans.

Comparison with jig dyeing is more than favourable; even at a conservative estimate production per man is 4–5 times as great.

With the Standfast machine, it is possible from both an economic and a practical point of view to dye any quantity of cloth from as little as one piece upwards. Several features help towards this end, but particularly the very small dyebath and the speed with which we can change shades. An example will make this point clearer. If one piece of cloth 100 yards long were dyed at, say, 40 yards per minute, the time required would be 2½ min. If the total time required for cleaning were 5 min. (which is our average time), the average speed for the whole operation would still be greater than 13 yards per minute, which is very much better than a similar piece could be dyed on the jig. On the other hand, with a process requiring several hours for cleaning, e.g. 2 hr., the average speed would be reduced to less than one yard per minute.

FASTNESS

The results of exhaustive tests show that the fastness to light is not affected in any way by this rapid dyeing, and colours dyed on the Standfast machine are equal to dyeings done by the usual methods. With regard to washing fastness we have

found that materials dyed by our process are in fact superior to those dyed by conventional methods, owing to the more complete fixation.

All the other fastnesses compare at least favourably.

Finally, I would like to express my appreciation to the Directors of Messrs. Standfast Dyers & Printers Ltd. for permission to give this paper.

Discussion

Mr. R. J. SMITH: Has it been found necessary to clean the actual metal because of any contamination by occluded dye particles or other foreign matter?

Mr. BOARDMAN: We do not find that the metal becomes contaminated with occluded dye particles. All impurities float to the surface, and the only cleaning necessary is that described. The wash liquor on the surface is, of course, renewed.

Mr. E. R. WILTSHIRE: To what extent is the production of heavy shades by the method described limited by the solubility of the dye?

Mr. BOARDMAN: We use rather higher concentrations of caustic and hydrosulphite than are normally employed, and also the temperature of reduction is much higher. Consequently, the solubility of the dye is increased. We have frequently dyed heavy shades of the order of 40% using various vat dyes, and have never had trouble with the dye solution being too concentrated.

Mr. J. HOLT: What is the tensile strength of cellulosic materials processed on the Standfast machine, as compared with the orthodox methods? One would presume that very much better results would be obtained by the new technique, but it would be interesting to have a general comparison.

Mr. BOARDMAN: The cloth is dyed in one passage through the machine, and dyeing is completed in, at the longest, a little over 7 sec. Prolonged immersion in the dye liquor is avoided, and there is no loss in tensile strength.

Mr. R. THORNTON: How critical is the head of molten metal? Can one expect differences on account of the legs of the works machine being approx. 5 ft., whereas the laboratory machine is roughly half size?

Mr. BOARDMAN: Providing the time of immersion is sufficient to give full fixation, the head of metal does not appear to be critical. Differences do not occur between the laboratory and works machines if the speed of the small machine is reduced to give similar immersion times to the works unit.

Mr. J. LAURIE: Is trouble experienced due to formation of a scum by oxidation of the surface of the metal?

Mr. BOARDMAN: There is no trouble due to oxidation, since there is no exposed metal surface.

NORTHERN IRELAND SECTION

Meeting held at the Queen's Hotel, Belfast, on 22nd February 1950, Mr. J. H. JACKSON in the chair

Contributions of Chemistry and Engineering to the Problems of Continuous Dyeing

R. G. FARGHER

This paper represents an expansion of a brief review[1] of the trends in German and American dyeing methods into a description of the development of continuous dyeing processes for cellulosic textiles, and thus provides a companion to the account of changes in bleaching practice[2]. The task is by no means easy, for dyeing presents so many more facets than bleaching that the scientific and technical approaches to its problems are converging much more slowly. Consequently, an appreciation of the position at any time is very subject to personal judgments.

There are many aspects that merit consideration. Thus, continuous dyeing makes an even greater demand on uniformity of materials and of their preparation than the established methods. It is fortunate, therefore, that our knowledge of the relations between the physical and chemical properties of cellulosic fibres and their response to dyeing now rests on a firm foundation. We are able to measure precisely the fineness of fibres, to relate fineness to surface area, and to predict the effects of both on behaviour during dyeing. We can measure the immaturity of cotton and assess its effects in dyeing. We can determine the degree of chemical modification of cellulosic fibres and relate it to behaviour during dyeing, and we now realise the importance of warp size residues in dyeing, particularly the dyeing of the man-made fibres.

In dyeing itself, progress has been made along three main lines. First, there is the fundamental approach to the mechanism of the processes; here the necessity to observe the effect of one variable at a time has produced a body of evidence so foreign to the practical dyer that the results have had as yet only a minor impact on the technical processes. Then there is the direct approach which seeks to attain objectives of immediate practical importance. Thus, direct dyes have been grouped according to salt and temperature controllability[3,4] and to time of half dyeing[5,6]; vat dyes have been classed on a temperature scale; the stability of the leuco compounds of the vat dyes, e.g. to hydrolysis and over-reduction, has been investigated[7]; and the use in dyeing of the hydrogen leuco compounds of the vat dyes has been explored[8]. Thirdly, there have been many attempts to lower the ratio of liquor to textile in technical dyeing and to permit the use of higher temperatures without discomfort[9].

Through these can be traced the gradual development of the modern continuous processes. Their prime object has been to increase productivity, but there are three other possibilities of even greater interest, namely more effective process control, greater uniformity of treatment, and the prospect of avoiding difficulties caused by the variation in response of dyes in the same class to temperature and concentration of electrolytes.

To these developments, both the chemist and the engineer have contributed. There are others which have come from the engineer alone, for example in the methods and control of padding and drying and in the control of tensions in the rope or in the open width. To complete the picture we must add the gradual development of objective methods for testing quality of dyeing by measurements of fastness to light, washing and rubbing, colour value, and penetration of the dye.

The dyeing of cellulosic materials is primarily a process of absorption, e.g. of a direct dye[10,11], of the sodium leuco compound of a vat dye[12], or of a reduced sulphur dye. The rate of absorption increases with the concentration of the dye, the temperature, and the concentration of electrolytes in the dye-bath. The dye also becomes less aggregated as the temperature rises, so it is assumed that the rate of dyeing may be very much greater near the boiling point than within the range over which measurements can be made conveniently. It is generally agreed that the advantages of a low liquor : goods ratio and a high temperature outweigh the disadvantages, and there have been many efforts to reduce the ratio of liquor to cloth in jig or wince dyeing machines. Some of the most interesting have been observed in Continental practice[9] and have as their object the elimination of dead space in the container. The total enclosure of jigs and winces aims to secure an economy in heat and a higher practicable dyeing temperature. The modern continuous processes are based on the assumption that, by reducing the ratio of liquor to textile to a minimum, correspondingly increasing the concentration of electrolytes, and raising the temperature of the cloth to about 212°F. as rapidly as possible, dyeing can be completed quickly enough to avoid complications arising from differences in stability or response to temperature of the dyes used. Naturally, there are accompanying disadvantages. Dyeing must be controlled exactly, for there can be no shade matching at the end of the process. It is also likely that the consumption of dye may be rather greater. Furthermore, the chances of concealing cloth irregularities and securing good penetration of dye may easily be lessened. Experience shows, however, that, with proper control, levelness and penetration are at least as good as after jig or wince dyeing.

The modern continuous dyeing processes embrace some or all of four stages, namely padding, intermediate drying, development, and aftertreatment.

PADDING

Continental machinery makers have advocated a continued refinement of the padding mangle and have produced several variants of the ordinary two- or three-bowl mangle with the ostensible objects of minimising waste of dye and securing more perfect impregnation of the fabric[13]. Only the simpler forms have come into common use, however, and the emphasis laid by some designers on the importance of nipping the cloth as it passes into or through the solution or dispersion of the dye, and on the adaptation of multibowl systems to hold the solution or dispersion of the dye, does not appear to have secured general approval. Following British practice, the bowls are usually 9–11 in. in diameter and are cambered in order to correct deformation under load; spring-loading is used with the more complex bowl systems.

In view of the rapid expansion of continuous dyeing in the United States, the strong contrast between American and Continental practice must be given due weight. In the United States the two- or three-bowl mangle is used almost exclusively, and the only important new feature is that a uniform nip is secured by pneumatic or hydraulic loading of large rubber and stainless-steel bowls up to 20 in. in diameter[1]. The rubber bowls are generally harder and the loading rather higher than elsewhere. Microsetting is employed to secure the accurate and reproducible nip expression which is so important in continuous dyeing.

The skew-setting of bowls[14], as an alternative to cambering, has made little progress anywhere, probably because of the attendant additional wear on bearings. In general, it may be concluded that the problem of the best difference in hardness of the bowls in relation to their diameter and loading still awaits solution.

INTERMEDIATE DRYING

There is still a considerable divergence of opinion on whether or how this process should be conducted. When dyeing is being carried out continuously and not in stages, however, drying is often omitted with vat dyes in pale shades. Esters of leuco vat dyes and the Naphtol components of azoic colouring matters are usually dried after padding, irrespective of the depth of shade required. Intermediate drying is unnecessary, of course, with direct, reduced vat, and reduced sulphur dyes, which may, however, be applied from two pads instead of one. When sulphur dyes are applied as dispersed pigments[15], they may be dried before passing through the reducing pad. The commonest method of drying is to pass through a chamber heated by circulation of hot air, and very rapid drying is avoided with all save the most uniformly woven fabrics.

Advantages are now being claimed, however, for superheated vapour drying[16], particularly with thin or reedy cloths. In this method, the air present in the dryer at the start of operations is quickly replaced by the steam given off by the cloth during drying, and this steam is superheated by gilled heat units placed within the chamber. This makes for economy in heat energy, but it is also claimed that there is less migration of dye from the closer to the more open portions of the cloth, which ordinarily tend to dry more rapidly, and that the danger of overdrying is minimised considerably.

DEVELOPMENT

The various methods, most of them primarily for the fixation of vat dyes on cellulosic materials, are based on the belief that if the temperature of the padded cloth be raised very rapidly to about 212°F., in absence of air and without undue loss of water, equilibrium will be established in a matter of seconds. There is little or no concrete evidence for this which can be studied dispassionately; therefore the statements must be judged very largely by the measure of practical achievement. There is, however, some evidence that with cellulosic fibres no material advantage is secured by aiming at a higher temperature[17], but that, on the other hand, temperatures up to at least 280°F. may be employed usefully in dyeing woollen and wool–cotton union cloths, with which equilibrium is reached more slowly[18].

The process worked out by S. H. Williams[15] of the General Dyestuffs Corporation is an ingenious development from the older continuous dyeing units such as the open ranges used in this country and the "booster boxes" used in the United States, and has overcome successfully many of their weak points. In the Williams unit the cloth passes down and up narrow vertical compartments separated by a heater unit and baffles, which occupy a large proportion of the space and ensure that the desired temperature is maintained. The baffles can be lifted out for cleaning. The reducing liquor is carried forward by the passage of the cloth through the narrow compartments, and overflows from the last compartment back to the first. It is revivified as required by continuous controlled additions of solid sodium hydrosulphite and a strong solution of caustic soda. A single unit is generally used for pale or medium shades, and two units in series for full shades.

The advantages of the unit are that it is compact and amenable to control, and, with long runs, the ratio of liquor to cloth processed is very low. The distance between the running cloth and the heater units or baffles is less than ¼ in., and so the passage of the cloth induces a turbulent flow of the liquor, which is claimed to assist speed and uniformity of dyeing. Its disadvantages are common to all processes in which the cloth is passed through a hot alkaline reducing liquor after pigment-padding. It is necessary to determine for each dye the equilibrium between removal from the cloth and recovery from the liquor in the unit[19]. Further, if the temperature is maintained at 212°F., in order to attain the maximum rate of dyeing, over-reduction or hydrolysis of some vat dyes in the unit may affect the shade of the dyeing. To avoid these difficulties, the unit is often used at a temperature of about 180°F., and the addition of a white dextrin is recommended to prevent over-reduction, particularly of vat blues[20]. The rate of passage of the cloth is diminished correspondingly. With vat dyes, the unit has been most successful with long runs in pale or medium shades; it is also approved for applying sulphur dyes by any of three methods, namely padding with the reduced dye followed by development in the unit; dyeing in the unit without padding; or padding with dispersed dyes which are afterwards fixed in the unit. Sometimes the possibility of using a temperature below 212°F. may be a definite advantage; thus, some measure of success is claimed in dyeing cloths containing spun rayon mixed with wool, provided that the dyes used are absorbed at approximately the same rate[15]. The unit has not proved successful in tinting with vat dyes prints containing discharges.

The processes sponsored by E.I. du Pont de Nemours & Co. Inc. and by I.G. Farbenindustrie A.-G. are based on the use of a steamer. In the Du Pont system, the developing unit is an adaptation of the aniline black ager in stainless steel. The steam box in the roof is replaced by spot-welded continuous stainless-steel coils, the carrying rollers are of stainless steel, and the cloth is passed through a liquid seal and between horizontally opposed bowls as it leaves the unit. The units are designed to permit the use of liquid "boosters" if they are needed. The temperature inside the unit must be maintained at or slightly above 212°F.

A possible weakness of the process is that the rate of rise of temperature of the cloth in the steamer may be too low. Despite its importance, there is still no proven method for recording the surface temperature of cloth in a steamer. Quite recently, however, a parabolic mirror with a thermocouple placed at the focal point[21] has been used to collect the radiation from printed cloth in a vat ager and so measure the rate of rise of temperature of the cloth; it did not reach 212°F. until after about 15 sec. As the rise of temperature of a cloth containing nearly its own weight of water is likely to be appreciably slower, dyeing in the steamer may well be taking place at a temperature only gradually approaching 212°F., even when the duration of treatment is increased to 20–30 sec. This may explain why comparatively little trouble has been experienced through over-reduction or hydrolysis of vat dyes and why the duration of treatment is often lengthened to 20 sec. or more.

The German process[8,22] may have aimed to heat the padded cloth more rapidly. The steamer is about 8 ft. long and 4 ft. 6 in. high, and holds seven or eight horizontal layers of cloth. It is heated by electrical elements at the top and by steam at the sides. The temperature is first raised to 360°F., and then steam is passed in to remove air. During the passage of the padded cloth the temperature inside the unit is maintained at about 265°F., so the process is conducted in an atmosphere of superheated steam. As the cloth passes from the top to the bottom of the steamer it comes close enough to the electrically heated elements at the beginning of the run to suggest that there may be some radiant heating. Furthermore, the process appears to have been used principally, if not entirely, with the hydrogen leuco compounds of selected vat dyes. From this, it may be inferred that experience has been predominantly with pale shades. I.G. did not advance the process for use with sulphur dyes. Instead, they recommended padding with the reduced dyes[23], followed by a passage through the air, rinsing, and oxidation with chromic acid. To

assist in selecting dyes suitable for use together, they grouped the available sulphur dyes according to the rate of absorption by the fibre. The limitations of the method are well understood in this country.

The use of containers filled with low-melting, fusible alloys[24] appears to have been examined in Germany both for drying and baking and as a possible means for fixing vat and direct dyes; there is, however, no evidence that the stage of technical application was reached. The use of fusible alloys has also been investigated in this country[25], and has proved to have a place in the development of vat and other dyes. The cloth may be pigment-padded and then passed through a reducing bath into the metal bath; or passed through the reduced vat straight into the metal bath; or the metal bath may be used as the developing unit after pigment-padding, drying, and passage through the reducing pad. It is claimed that well penetrated level dyeings of good fastness are obtained on a wide variety of fabrics with a duration of development of 10–15 sec. at about 230°F., and that the process is equally applicable with dyes which are usually applied at low or high temperatures. An important advantage of the metal bath is that the temperature of the cloth may rise more quickly than in the other processes through the rapid transfer of heat from metal to cloth. Moreover, the passage of the cloth from the reducing liquor immediately into the metal bath should prevent the formation of a film of air on the cloth, and bring the solution of the dye into intimate contact with the cloth without dilution or evaporation. A weak point would seem to be the limited application to sulphur dyes. The metal bath does, however, suggest the direction in which progress must be sought if rapid attainment of the nominal temperature of reaction is a decisive factor in continuous dyeing.

Two other methods may be mentioned briefly. One is the Multilap continuous processing machine, designed by Du Pont for the continuous dyeing of fabrics which are too extensible or too fragile to stand the tensions imposed by the other processes. They recommend it particularly for applying direct, acid, sulphur, or vat dyes to fabrics containing more than one fibre. The process consists in padding followed by a passage through an enclosed chamber in which the cloth moves alternately through a dye liquor and over a slatted reel, on which it is steamed until a suitable number of laps has been built up to secure the desired duration of treatment. On the reel, the laps lie tightly upon one another, with the exception of the last to come through the liquor, which is separated by passing over a roller at the top. Finally, the cloth is turned through an angle of 90° over a rigid rail and passes out of the chamber through draw rollers, from which the excess liquor is returned to the machine down a sloping drip tray. Possibly because of the large volume of liquor employed, the industrial use of the process has been very limited, and then principally to woollen fabrics or fabrics containing wool together with nylon or viscose or acetate rayon.

The other method is the technique of the Bachmann Uxbridge Worsted Corporation[17] for dyeing under pressure at temperatures up to 280°F. Little is known of the process*, but it has been stated to have useful applications in the dyeing of fibres, such as wool, which require a long time for the diffusion of the dye into the individual fibres under ordinary conditions. With suitable dyes, the speed of dyeing can be increased sufficiently to come into line with the other continuous processes.

AFTERTREATMENT

None of the descriptions of continuous dyeing processes affords any suggestion for the aftertreatment of the leuco compounds of those vat dyes that are unlikely to be re-oxidised completely by the more or less perfunctory oxidation, soaping, and washing which are possible in an open range operated at a high speed. It is possible that such dyes are avoided whenever possible, and that, when they must be used, they receive an additional, non-continuous treatment.

By contrast, washing at high speed is receiving considerable attention. In addition to the control of warpway tension by fitting a separate motor and compensator to each section of a continuous range and to the application, by the Spooner Dryer & Engineering Co. of a high-pressure spray simultaneously to the face and back of the cloth, there are at least two later developments. The first is the general application in the United States of the Williams unit for washing after dyeing, two units in series replacing four or even five open boxes. The second is the introduction of the Tensitrol principle to open-width or rope washing machines by the Rodney Hunt Machine Co. with the dual purpose of increasing efficiency of washing and preventing the building up of tension[27]. In these machines, the top rollers are set in low-friction bearings and the bottom rollers are driven at a slightly greater speed than that at which the cloth is drawn through the machine. Consequently, if tension develops locally through shrinkage, the speed of the following cloth is increased by the bottom rollers. The machines are claimed to ensure very thorough washing at high speed and to economise in water. It has also been suggested that the principle might find a useful application in continuous dyeing processes which employ the liquid "booster".

CONCLUSION

Continuous dyeing thus presents many interesting problems which deserve consideration; some of them have been realised for a long time, but others may be novel. There are, for example, the improvement of the padding mangle, and the suggestion[25] that the padding mangle may be discarded without detriment to quality of dyeing or control of the process. This may prove of particular interest in relation to the continuous dyeing of warps. There is also the problem of how best to dry between the pigment and reducing

* Since this paper was submitted for publication, a comprehensive account of the process has appeared[26]. Attention may be directed particularly to the system of pressure-sealing rolls used in the machine.

pads. In the development processes, there is the measure of importance which should be attached to the speed with which the cloth attains the temperature at which dyeing is being nominally conducted. This limits the compactness of the vessel in relation to speed of running and also bears on the problems of dye stability, uniformity of dyeing, penetration of dye and proportion of the dye employed usefully in continuous as compared with non-continuous processes.

Finally, there are the problems of reoxidising completely the less easily oxidised leuco vats and of soaping and washing sufficiently thoroughly at a high speed without unduly lengthening the open range or its more modern equivalents.

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[20] A.A.T.C.C. Piedmont Section, *Amer. Dyestuff Rep.*, **38**, P 213 (1949).
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[22] *BIOS Overall Report* 13, p. 62.
[23] *FIAT* 644, p. 54.
[24] *BIOS* 514, p. 62.
[25] Morton Sundour Fabrics Ltd., Hannay, and Kilby, *B.P.* 620,584 (1949); Boardman, J.S.D.C., **66**, 397 (Aug. 1950).
[26] Robinson and Zimmerman, *Amer. Dyestuff Rep.*, **39**, P 250 (17th April 1950).
[27] Rodney Hunt Machine Co., *B.P.* 631,279 (1949).
[28] Marr, J.S.D.C., **66**, 108 (Feb. 1950).

Discussion

Mr. D. A. DERRETT-SMITH: Has any continuous method been developed for yarn dyeing?

Dr. FARGHER: Continuous warp dyeing in single- or multi-box machines has been practised for many years, and a very good account of the methods has been given by G. S. Marr[28]. The newer methods are stated to be applicable to warps, but apparently their use for this purpose has, so far, been very limited, probably because of the widening application of beam dyeing.

Mr. J. PORTER: Can relatively heavy linen piece goods, such as dress materials and suitings, be dyed successfully with vat dyes by any of the continuous processes? Can good penetration be obtained?

Dr. FARGHER: The processes are applied successfully to cotton goods of similar weight and texture. I have seen only experimental dyeings on linen dress goods; they were level and well penetrated.

Mr. N. HINDSHAW: Is the standard of matching in the U.S.A. by the continuous dyeing methods as high as by the ordinary methods used in this country?

Dr. FARGHER: The standard of matching depends upon the quality of scientific and technical control. Where both are high, matching in continuous dyeing compares favourably with matching in dyeing on the jig or wince.

Mr. J. PORTER: Is the acid–leuco method of vat dyeing employed extensively in continuous dyeing in the U.S.A., and what degree of success has been obtained?

Dr. FARGHER: The acid–leuco method is sometimes employed, principally in dyeing pale shades. It is applicable only with dyes or mixtures of dyes which give very fine dispersions at the required concentrations. There may be some improvement in levelness, penetration, and fastness to rubbing. The results appear to be directing attention to the production of vat dyes sufficiently finely divided to give dispersions with an average particle size of less than 2 μ.

Mr. J. KERSHAW: What are the possibilities of pigment padding with vat dyes in organic solvents instead of water?

Dr. FARGHER: There are very few good solvents for vat dyes. Their application in this way would be an advantage only if the particle size remained very small and reduction took place correspondingly rapidly. So far, the principal applications of organic solvents have been in promoting or restraining the swelling of particular fibres and in the control of rate of dyeing.

Mr. F. L. DURRANS: Is the liquid booster much used in the pad–steam process?

Dr. FARGHER: In my experience it is generally avoided for the reasons given (p. 407). It appears, however, that the use of one or more liquid boosters maintained considerably below the temperature of the steamer by external cooling is now being advocated. There are evident weaknesses in this procedure, e.g. condensation and lowering of the temperature of the cloth, which might be expected to slow down the rate of dyeing.

Dr. B. C. GEE: Is drying necessary after padding with the esters of leuco vat dyes to achieve the best results?

Dr. FARGHER: Drying is by no means general. Superheated vapour drying is, however, recommended with thin reedy cloths.

LEEDS JUNIOR BRANCH

Meeting held at the University of Leeds on 24th January 1950, Mr. C. L. BIRD in the chair

Recent Trends in the Search for New Azo Dyes
III—Direct Dyes for Cotton

A. H. KNIGHT

Introduction

The direct cotton dyes, which are mostly of the azo class of colouring matters, have been defined as water-soluble dyes which have a strong affinity for cotton and are absorbed directly from their neutral or slightly alkaline solutions[1]. Dyebath exhaustion is usually promoted by addition of an inorganic salt such as Glauber's salt. They also find wide application in textile printing, particularly in discharge printing on cellulosic fibres.

The direct dyes still represent a very considerable proportion of the world production of dyes. Their importance has greatly increased since the first world war, as the result both of the increased production of regenerated cellulose or viscose rayon, and of improvements in the quality and consistency of manufacture of such rayon. The size of the potential business in direct dyes for cellulosic fibres in contrast to that in dyes for wool can be appreciated by considering the estimates in Table I of world production for 1937 and 1947 of cotton, viscose, wool, and silk on the one hand and of direct, acid, and chrome dyes on the other, the latter two classes of dyes being used mainly for colouring wool and silk. Not all of these quantities of raw fibres, however, reach the consumer in the coloured state.

TABLE I

Estimated World Production of the Main Fibres[1a] and of Direct, Acid, and Chrome Dyes[1b]

(metric tons)

	1937	1947
Raw cotton	8,000,000	5,020,000
Viscose rayon	480,000	678,600
Scoured wool	1,034,000	1,036,000
Raw silk	54,500	15,000
Direct dyes	64,400	43,200
Acid dyes	34,800	29,300
Chrome dyes	10,500	12,400

It must be remembered, of course, that the direct dyes represent only one of the classes used for colouring cotton, others being the basic, sulphur, vat, and azoic dyes. The estimated world production for all these latter classes (including Indigo) is 137,700 tons for 1937 and 108,200 tons for 1947. Thus, the direct dyes represented approx. 31% of total cotton-dye tonnage in 1937 and approx. 28% in 1947.

It is obvious that, in a business of the magnitude involved in the colouring of cotton and viscose rayon by any of the possible methods employing the various classes of suitable dyes, there is likely to be keen competition between the makers of the necessary commercial dyes both as regards sales of well established products and in the fields of research necessary to effect continuous improvements in hue and fastness properties by discoveries of new dyes, improved or new methods for their application, or both. This has certainly been the case with azo direct dyes for cotton and viscose, and this paper will describe a few of the directions in which dye manufacturers have conducted their researches on this class of dye during the last thirty years in the search for new and improved products and methods of application. The main objectives have been dyes of high light fastness or high wet fastness, and much effort has been devoted to attempts to combine these properties in the finally coloured material. As regards hues, whilst better dyes of all hues ranging from yellow to blue, brown, and grey have been sought, a very important objective has been the discovery of satisfactory greenish-blue and green dyes. A more recent objective has been the discovery of further direct dyes which on viscose rayon are stable to the various crease-resisting processes now in use. Of the present-day ranges of fast-to-light direct dyes there may be mentioned as examples the Durazol (ICI), Sirius Supra (IG), Chlorantine Fast (SCI, now Ciba, and CAC), and Pontamine Fast (DuP) ranges.

The main sources on which an enquirer has to rely for chemical information on a topic such as the present one are the dye manufacturers' published patent specifications. There is, however, a vast amount of information now published in BIOS reports and microfilms concerning the constitutions of direct dyes manufactured in Germany by the I.G. Farbenindustrie A.-G. and the research work carried out by that organisation on direct dyes during 1936–1941. Judging from patent specifications and marketed novelties, the greatest research activity on direct dyes between the two world wars was shown by the I.G. and by the Swiss firms, particularly Ciba (formerly the Society of Chemical Industry in Basle). In Britain, some contributions were made by Imperial Chemical Industries Ltd., especially in connection with dyes of a rather low order of cotton affinity suitable for the satisfactory dyeing of irregular viscose, from which the Icyl range was developed. Of American dye-manufacturing firms, only E. I. du Pont de Nemours & Co. have taken out many patents in this field. Very few inventions have appeared from French and Italian dyemaking firms. The Swiss firms Ciba, Geigy, and Sandoz, who during the recent war were able to maintain their research activity, continued to prosecute actively their investigations in this field of azo colour chemistry, and to-day are still the most active of the world's dyemakers therein.

A Brief Review of the "Art" up to about 1920

Brief mention will be made of the main types of configuration used for the earlier direct dyes, many of which are still widely used where cheapness combined with a moderate order of wet and light fastness are the main requirements.

Firstly, there is the azo class of dyes based on benzidine and its 3:3′-dimethyl and 3:3′-dimethoxy derivatives. These included disazo, trisazo, and more complex azo dyes, and they provided a hue range from yellow to black. The disazo members, some of which were symmetrical and others unsymmetrical with respect to the coupling components used, lacked greenish yellows and full blacks. Yellows were obtained by use of other diamines, such as 4:4′-diaminodiphenylurea and 4:4′-diaminostilbene derivatives. Blacks, as well as green and deep brown dyes, were obtained from trisazo and tetrakisazo structures based on benzidine and also on *p*-phenylenediamine. The following examples illustrate the types used and the hues obtained—

YELLOW (*C.I.* 410)

Salicylic acid←Benzidine→Salicylic acid

RED (Congo Red, *C.I.* 370)

Naphthionic acid←Benzidine→Naphthionic acid

RED (*C.I.* 419)

Salicylic acid←Benzidine $\xrightarrow{\text{Acid}}$ γ acid

BLUE (*C.I.* 406)

H acid $\xleftarrow{\text{Alkali}}$ Benzidine $\xrightarrow{\text{Alkali}}$ H acid

GREENISH BLUE (Sky Blue FF, *C.I.* 518)

2S acid $\xleftarrow{\text{Alkali}}$ Dianisidine $\xrightarrow{\text{Alkali}}$ 2S acid

DEEP BROWN (*C.I.* 420)

Salicylic acid←Benzidine $\xrightarrow{\text{Alkali}}$ γ acid

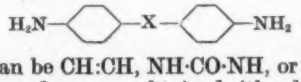
BLACK (*C.I.* 581)

m-Phenylenediamine←Benzidine $\xrightarrow{\text{Acid}}$ H acid $\xleftarrow{\text{Alkali}}$ Aniline

GREEN (*C.I.* 594)

Salicylic acid←Benzidine $\xrightarrow{\text{Alkali}}$ H acid $\xleftarrow{\text{Acid}}$ *p*-Nitroaniline

Secondly, there are the stilbene-azo dyes, a very important section of the rather small class of dyes derived from what are known as *bridged* diamines of general formula—



where X can be CH:CH, NH·CO·NH, or NH. The early stilbene dyes were obtained either by tetrazotising 4:4′-diaminostilbene-2:2′-disulphonic acid and coupling with two molecules of a coupling component, as for the indicator Brilliant Yellow (*C.I.* 364) from two molecules of phenol, the *OO′*-diethylation product of which is the important dye Chrysophenine G (*C.I.* 365); or by caustic alkaline condensations of 4:4′-dinitrostilbene-2:2′-disulphonic acid (or its precursors *p*-nitrotoluene-*o*-sulphonic acid and 4:4′-dinitrodibenzyl-2:2′-disulphonic acid) with aromatic amines, including aminoazo compounds. Chrysophenine is a valuable bright yellow direct cotton dye; whilst the condensation products, which are rarely homogeneous, yielded dyeings limited to yellow, orange, yellowish brown, and scarlet, but having, in the main, high light fastness (5–6 on the S.D.C. 1–8 scale), and good fastness to washing, acids, alkalis, and chlorine. These hues and fastness properties could be modified by the presence in the reaction mixtures of reducing agents such as glucose and by treatment of the reaction products with oxidising agents such as sodium hypochlorite. Examples of such old-established condensation products are Chlorazol Yellow G (*C.I.* 620), Chlorazol Fast Orange D (*C.I.* 621), and Chlorazol Fast Yellow FG (*C.I.* 622) based on *p*-nitrotoluene-*o*-sulphonic acid alone; and Curcuphenine (*C.I.* 634), an alkaline condensation product from *p*-nitrotoluene-*o*-sulphonic acid and dehydrothio-*p*-toluidinesulphonic acid.

Thirdly, there is the important group of disazo and trisazo dyes having J acid (2-amino-5-naphthol-7-sulphonic acid) or an *N*-derivative of J acid as E in the general formulæ A→M→E and A→M¹→M²→E, and the disazo dyes from J acid-urea (carbonyl-J acid) or from di-J acid as Z in the formula A¹→Z←A² (A¹ and A² either the same or different). J Acid was found to be outstanding in its contribution to the affinity for cotton of the azo dyes of which it was a component.

The secondary disazo class A→M→E provided level-dyeing, bright red, violet, and blue dyes of medium light fastness (4–5), of which the following may be quoted as examples—

BLUISH RED (*C.I.* 278)

Sulphanilic acid→Aniline→*N*-Benzoyl-J acid

BLUE (*C.I.* 319)

H acid→α-Naphthylamine→*N*-Phenyl-J acid

The trisazo class A→M¹→M²→E, having a second middle component, gave hues displaced towards the green, so that pure blue and greenish-blue dyes were obtained, and even bluish greens by suitable selection of M¹ as a 1-amino-2-alkoxy-naphthalene-6(or 7)-sulphonic acid. In the latter case the coupling energies of the unstable diazo compounds of the disazos A→M→2-alkoxy-Cleve acid were found to be very low in alkaline sodium carbonate or ammonia solution. It was later discovered that couplings of such diazo compounds with J acid and its *N*-derivatives were much improved by carrying them out in the presence of pyridine[2] or ammoniacal acetone[3], whereby reasonable yields and purities of the final dyes were obtained. Examples of dyes of this trisazo class are—

BLUE (*C.I.* 533)

Aniline→1:6-Cleve acid→1:6-Cleve acid $\xrightarrow{\text{Alkali}}$ J acid

GREENISH BLUE

Aniline-2:5-disulphonic acid→α-Naphthylamine→
2-Methoxy-1:6-Cleve acid→Phenyl-J acid

Mention has already been made of the urea from J acid (carbonyl-J acid) as a coupling component. This compound can couple successively with two molecules of diazo compound, so that it permits the preparation of either symmetrical or unsymmetrical disazo or polyazo dyes. A typical example is the bluish-scarlet dye—

C.I. 327

Aniline→Carbonyl-J acid←*p*-Aminoacetanilide

whilst the symmetrical disazo dye from diazobenzene is an orange[4]. As a class, the simple disazo dyes of this type from aniline and naphthylamine diazo components furnish orange and red dyeings on cotton of similar washing fastness to that of the benzidine red dyes, but they have rather superior light fastness and much superior fastness to acids. Corresponding dyes from di-J acid, which is obtained by boiling two molecules of J acid with sodium sulphite and couples with two molecules of a diazo compound in a similar manner to carbonyl-J acid, are bluer but of lower affinity and washing and light fastness than those from carbonyl-J acid. Ureas of the important 1:8-aminonaphtholsulphonic acids, H, K, S, and 2S, cannot be made by phosgenation of these acids. Apparently ring formation occurs by reaction of the phosgene with the *peri* amino and hydroxyl groups.

Fourthly, there is the class of dyes which may be said to be based on 4:4′-diaminodiphenylurea. In practice, these dyes are usually made by phosgenating the corresponding aminoazo compound rather than from this diamine and its derivatives, which tend to be sparingly soluble. Important members are the yellow phosgenation product from 4-amino-4′-hydroxy-3′-carboxyazobenzene (*C.I.* 346), the yellow urea from *m*-aminobenzoic acid→*o*-anisidine (*C.I.* 349), and the pink dye obtained by phosgenating *p*-phenylenediamine-*o*-sulphonic acid $\xrightarrow{\text{Acid}}$ γ acid (*C.I.* 353). These dyes possess good to very good washing fastness, while light fastness is generally good and sometimes quite high.

Fifthly, there are polyazo dyes of grey and black hues, many of which involve the use of γ acid (2-amino-8-naphthol-6-sulphonic acid) as a coupling component. γ Acid contributes less than J acid to the affinity of derived dyes. When coupled *ortho* to its amino group (acid coupling) it leads to good light fastness, and when coupled *ortho* to the hydroxyl group (alkaline coupling) it is a useful middle component and is so used for the Pluto (By) and Columbia (A) Blacks. Examples of grey and black polyazo dyes are—

BLACK[5]

p-Aminosalicylic acid→*α*-Naphthylamine $\xrightarrow{\text{Alkali}}$ γ acid

BLACK[6]

p-Phenylenediamine→Cresidine $\xrightarrow{\text{Alkali}}$ γ acid

LIGHT GREY[7]

2-Naphthylamine-4:8-disulphonic acid
→*α*-Naphthylamine→Cleve acid $\xrightarrow{\text{Alkali}}$ γ acid

BLACK (*C.I.* 539)

Cleve acid←*p*-Phenylenediamine $\xrightarrow{\text{Alkali}}$
γ acid→*m*-Phenylenediamine

Some of these dyes having alkaline-coupled γ acid as final component are diazotised on the fibre and coupled to components devoid of solubilising groups such as β-naphthol, *m*-phenylenediamine, or phenylmethylpyrazolone. The hues are modified and the wet fastness is increased.

This process of diazotisation and coupling (development) on the fibre with compounds free from water-solubilising groups was invented by A. G. Green in 1887[8]. The increased washing fastness arises from the increased cotton affinity which is usually contributed by introduction of an extra arylazo group and by the production of a dye molecule of relatively lower water-solubility. There are manufactured a number of developing cotton or *ingrain* dyes which have little or no value as direct dyes and are made specifically for this after-treatment process. These include the Rosanthrenes (Ciba and CAC), which are probably the best known examples of monoazo dyes possessing cotton affinity, for which they depend on the use of an aminobenzoyl-J acid as coupling component. β-Naphthol, phenylmethylpyrazolone, and *m*-phenylene(or toluylene)diamine are probably the most widely used "developers" for these dyes, the first for oranges, reds, and blues, the second for yellows and greens, and the last for browns and blacks. Good dischargeability and, for the oranges and reds, brightness are important commercial requirements for this class of dye. Light fastness of the developed dye is usually poor with the lighter hues but quite good in the case of some of the navies and blacks. Examples are—

ORANGE (*C.I.* 324*a*)

Aniline→*m*-Aminobenzoyl-J acid

ORANGE (*C.I.* 324)

Aniline→*m*-Aminobenzoyl-*m*-aminobenzoyl-J acid

RED[9]

4-Aminoazobenzene-4′-sulphonic acid→
p-Aminobenzoyl-J acid

BLUE[10]

2-Naphthylamine-4:8-disulphonic acid→
α-Naphthylamine→Cleve acid→Cresidine

GREEN[11]

3-Chloro-2-aminotoluene-5-sulphonic acid→
2-Ethoxy-1:6-Cleve acid→*p*-Aminobenzoyl-H acid

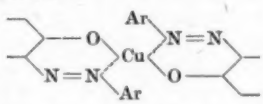
The hues quoted for the first four dyes are those obtained when β-naphthol is used as developer, whilst that for the last dye is obtained by development with phenylmethylpyrazolone.

The complementary use of the direct dye as coupling component was introduced alongside the ingrain process, and similarly leads to products of reduced water-solubility. The *azoic* or "ice-colour" process, in which a completely insoluble pigment is formed on the fibre, can be considered as the ultimate development of both these processes. This last process consists essentially in producing water-insoluble dyes on the fibre by impregnating the cotton with a solution of the sodium salt of a coupling component such as β-naphthol or an arylide of 2-hydroxy-3-naphthoic acid (a Naphtol (IG) or a Brenthol (ICI)) and subsequently passing the lightly rinsed material through a bath containing a solution of a suitable diazo compound, usually with an acid-binder present, which results in the formation of the azo pigment. The full brightness and light fastness of such colorations are "developed" by rinsing the cotton to remove loose pigment from the surface and immersing it in a boiling soap solution. By suitable choice of diazo component and coupler a very wide range of hues can now be obtained: some of the colorations have fastness properties comparable with those of vat dyes.

Another long-established method for increasing the washing fastness of certain direct dyes, without necessarily effecting any improvement in light fastness, is aftertreatment of dyes derived from *m*-phenylenediamine, *m*-aminophenol, or resorcinol as coupling component with formaldehyde, sparingly soluble condensation products being thereby formed. The old Vulcan dyes of Levinstein Ltd.[12] and the Benzoform (IG) dyes were marketed for such aftertreatment.

Many years ago it was found that improvement of the light and/or wet fastness of certain direct dyes, particularly those containing salicylic acid residues, e.g. *C.I.* 420 (see p. 411), could be effected by treating them on the fibre with salts containing metals of atomic weight 50–70. Copper salts were particularly useful for increasing light fastness and chromium salts for wet fastness.

In many cases a marked change of hue, of a bathochromic and dulling nature, accompanied such aftertreatment. Some dyes other than those from salicylic acid were amenable to improvement in light and washing fastness by such a process. However, in many such cases, e.g. the aftercoppering of Chlorazol Sky Blue FF (*C.I.* 518, see p. 411), the effect was diminished or removed entirely by alkaline washing treatments, indicating that the copper compound formed was either a salt of a sulphonic acid or a loose co-ordination complex involving the azo group and the hydroxy group in *ortho* position to it, or both, the copper being removed by the alkaline treatments. The structural formulation—



which involves two molecules of parent monohydroxyazo compound, has been given by Drew and Landquist[13] for such copper complexes. It was later found that more stable products were produced by an aftercoppering treatment if the parent dyes contained *oo'*-dihydroxyazo or *o*-hydroxy-*o'*-carboxyazo configurations in their molecules. More will be said of such dyes later (pp. 418–420).

Some Developments of the Past 30-35 Years

Against the above background of "prior art", let us consider some of the developments in the chemistry and technology of azo direct dyes during the last thirty years or so. In my view, there have been only two major inventions in this field during that period, though a host of subsidiary inventions, some of considerable technical and commercial importance, have flowed from these two, and many others not connected with them have also been made and have led to profitable business for a number of dyemakers. Both of these two major inventions were made by the Society of Chemical Industry in Basle (now Ciba).

COPPER COMPLEXES OF DIRECT DYES

The first of these inventions was based on the discovery about 1915 that certain substantive *oo'*-dihydroxyazo dyes could be converted by copper salts or copper hydroxide into well defined copper compounds, soluble in water, from which the copper could not be precipitated by means of alkalis or ammonia. These copper-containing compounds would dye cotton from their aqueous solutions after the manner of the parent substantive dyes, but with a remarkable enhancement of light fastness and considerable improvement in fastness to acid and alkali. Copper-complex formation was usually accompanied by a change of hue. All these effects could be produced also by treating the parent substantive dyes on the fibre with copper salts. In Ciba's original patent specification[14] most of the *oo'*-dihydroxyazo structures were provided by the residue—

o-Amino-phenol(or -naphthol) $\xrightarrow{\text{Alkali}}$ J acid (or a derivative)

but dyes were also described from tetrazotised 3 : 3′ - dihydroxybenzidine, 3 : 3′ - diamino - 4 : 4′ - dihydroxydiphenylurea-5:5′-disulphonic acid, and other diamines containing hydroxyl groups *ortho* to the amino groups. Dis-, tris-, and tetrakis-azo structures were described containing one or more of the *oo'*-dihydroxyazo structures and providing for coppered dyes giving on cotton reds, violets, blues, greys, and blacks. Typical examples of the patent are given in Table II.

TABLE II

Parent Dye	Hues on Cotton— Parent Dye	Coppered Dye
2-Aminophenol-4-sulphonic acid→ Carbonyl-J acid←2-Aminophenol-4-sulphonic acid	Dull yellowish red	Blue–red
1-Amino-2-naphthol-4-sulphonic acid $\xrightarrow{\text{Alkali}}$ J acid→NW acid ...	Heliotrope	Reddish grey
o-Aminophenol→Carbonyl-J acid← Benzidine→NW acid	Violet–brown	Red–violet

A number of important dyes of this type have been patented during the last thirty years. I.C.I. have patented[15] the bluish-red copper-complex dye from—

(6-Chloro-2-aminophenol-4-sulphonic acid)$_2$⇄ Carbonyl-J acid

which is faster to light than the corresponding dyes from 2-aminophenol-4-sulphonic acid and 4-chloro-2-aminophenol. They have also patented[16] the corresponding copper-complex dye from di-J acid, which is a fast-to-light violet. The copper complex of—

(2-Aminophenol-4-sulphon-*N*-methylamide)$_2$⇄Di-J acid

was marketed by I.G. as Sirius Supra Violet BL[17]. More recently Ciba have patented[18] red to violet copperable disazo and trisazo dyes containing as diazo component one or more molecules of an arylide of 2-aminophenol-4-carboxylic acid, e.g.—

(2-Aminophenol-4-carboxyanilide)$_2$⇄Carbonyl-J acid

for a fast red–violet dye.

An important extension of this discovery was made by Ciba when they found that certain disazo dyes, obtained by alkaline coupling of tetrazotised dianisidine either with one molecule of J acid (or an *N*-alkyl, *N*-aryl, or *N*-acyl derivative thereof) and one molecule of a 1:8-aminonaphtholsulphonic acid or a derivative thereof, or with two molecules of J acid or a derivative thereof, could be coppered to

give substantive complexes which dyed cotton blues of very good fastness to light, alkali, and washing. Such dyes were patented[19] in 1917, and ten years later I.G. patented certain light- and wash-fast violet coppered dyes from diazotised *o*-alkoxyanilines and certain derivatives of J acid, e.g. carbonyl-J acid and di-J acid. About the same time I.G. found that copper complexes of *oo'*-dihydroxyazo compounds could be obtained by treating the corresponding *o*-alkoxy-*o'*-hydroxyazo compounds with copper compounds under conditions in which the alkyl groups contained in the alkoxy groups were split off[21]. In 1930 they applied this technique to certain disazo dyes from dianisidine. For example, the dye—

R acid←Dianisidine→*N*-*p*-Methoxyphenyl-J acid

was coppered with copper sulphate in weak sulphuric acid in an autoclave at 110–115°c. for about 20 hr. to give a blue very fast to light and fast to alkalis[22]. This type of coppering can be effected under widely varying conditions, depending on the constitution of the parent dye, and working under pressure is rarely necessary. If it is carried out in aqueous ammoniacal medium, methylamine is evolved, which can be readily detected by its smell. It is often advantageous to prepare *o*-methoxy-*o'*-hydroxyazo rather than the corresponding *oo'*-dihydroxyazo compounds for coppering, since the diazonium compounds of *o*-alkoxyaniline derivatives are usually much more vigorous couplers than those of the corresponding *o*-aminophenols. More rapid working, better yields, and greater purity of the uncoppered dyes therefore generally result from the use of the *o*-alkoxyarylamines. However, the coppering process usually takes a longer time to complete with an *o*-methoxy-*o'*-hydroxyazo than with the corresponding *oo'*-dihydroxyazo structure. A number of patents have been taken out describing improved techniques for coppering direct dyes containing *o*-methoxy-*o'*-hydroxyazo groups. Thus, the need for pressure is said by I.G. to be avoided by aqueous coppering in the presence of an organic base such as pyridine[23]. Coppering at 85–100°c. with an ammoniacal aqueous solution of a copper salt in presence of metallic copper is said by the Allied Chemical and Dye Corporation to give products which dye cotton brighter hues and stain fibres made of organic derivatives of cellulose less than do the products obtained by coppering in the absence of metallic copper[24]. The presence of aliphatic amines containing a hydroxyl group (e.g. diethanolamine) is said by Ciba to result in purer products and better yields in coppering *o*-alkoxy-*o'*-hydroxyazo dyes containing a sulpho group and at least two azo groups, particularly such dyes made from 1:8-aminonaphtholsulphonic acids as coupling components[25].

Much use has been made of *o*-methoxy-*o'*-hydroxyazo structures in synthesising fast-to-light copper-containing azo direct dyes. Thus, I.G. marketed the following copper complexes—

Sirius Supra Rubine BBL[26]

2-Anisidine-4-sulphonic acid→Carbonyl-J acid←2-Anisidine-4-sulphonic acid

Sirius Supra Blue FBGL[27]

1-Naphthol-3:8-disulphonic acid←Dianisidine→*N*-Phenyl-J acid

whilst I.C.I. patented[28] in 1934 the greenish-blue copper complex of the important blue dye Chlorazol Sky Blue FF (*C.I.* 518, p. 411). There has been much further patenting of coppered dyes from dianisidine in recent years[29], particularly of extensions of the above symmetrical and unsymmetrical disazo types. The main objective here appears to have been new fast-to-light blue dyes. Unlike most blue direct cotton dyes, some of these are alleged to retain their good light fastness on viscose rayon when the dyed viscose is submitted to a crease-resisting process by treatment with a resinous, e.g. urea–formaldehyde, condensation product. The copper complex of—

R acid←Dianisidine→2S acid

is said to be a dye of this type[30].

In 1920, Bayer disclosed that dyes obtained by coupling two molecules of diazotised anthranilic acid or a derivative thereof with di-J acid could be converted in substance into copper complexes which gave red–violet dyeings on cotton of excellent fastness to light[31]. This invention paved the way for many later inventions of fast-to-light dyes which owe their fastness largely to the presence in the molecule of a coppered *o*-hydroxy-*o'*-carboxyazo structure. Ciba later covered the manufacture of corresponding coppered dyes from carbonyl-J acid[32], the parent from two molecules of diazotised anthranilic acid itself being an exceedingly fast-to-light red–brown dye. The diamines benzidine-3:3'-dicarboxylic acid, 4:4'-diaminodiphenylurea-3:3'-dicarboxylic acid, azoanthranilic acid[33], and 4:4'-diaminostilbene-3:3'-dicarboxylic acid[34], representing substantive derivatives of anthranilic acid, have also been used as tetrazo components for metallisable dyes containing *o*-hydroxy-*o'*-carboxyazo structures. Thus, Sirius Supra Blue 3RL (IG)[35] is the copper complex of—

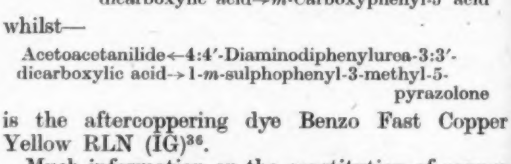
m-Carboxyphenyl-J acid←Benzidine-3:3'-dicarboxylic acid→*m*-Carboxyphenyl-J acid

whilst—

Acetoacetanilide←4:4'-Diaminodiphenylurea-3:3'-dicarboxylic acid→1-*m*-sulphophenyl-3-methyl-5-pyrazolone

is the aftercoppering dye Benzo Fast Copper Yellow RLN (IG)[36].

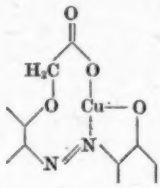
Much information on the constitution of copper complexes of azo dyes has been provided by the work of Pfeiffer[37], Drew[38], and their respective coworkers. As examples of the types of structure obtained by coppering *oo'*-dihydroxyazo and *o*-hydroxy-*o'*-carboxyazo compounds we can take the simple cases of *o*-aminophenol→*β*-naphthol and anthranilic acid→*β*-naphthol, thus—



In the first case an *ortho*-condensed system consisting of a six- and a five-membered ring is formed;

in the second case, one consisting of two six-membered rings. In each case the copper atom and a nitrogen of the azo group provide the linkage common to both rings.

Another metallisable structure, which has found application in dyes for aftercoppering on the fibre (see pp. 418, 419), is the *o*-hydroxy-*o'*-carboxymethoxyazo residue, which gives rise to an internal complex of the type—



It may be mentioned here that, whereas with mordant wool dyes chromium is the metal generally employed for chelation, with direct cotton dyes copper is usually preferred. However, an after-treatment with chromium salts of direct dyes containing salicylic acid residues to increase wet fastness properties (but not necessarily light fastness) is sometimes given, as in the Benzo Fast Chrome (IG) dyes, which are used not only as straight dyes but mainly as components of union metachrome dyes for mixed textile fabrics. An example is—

BENZO FAST CHROME BLUE FG[39]

5-Amino-2-hydroxy-3-sulphobenzoic acid→1:7-Cleve acid→1:6-Cleve acid→Phenyl-J acid

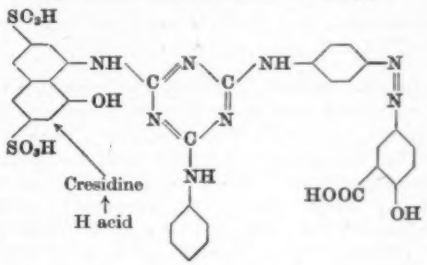
CYANURIC DYES

The second major advance in azo dyes for cotton was the discovery in 1922–1923 by Ciba of the ability of the 1:3:5-trihalogenotriazines, cyanuric bromide and chloride, to replace their halogen atoms in stepwise fashion by the residues of primary and secondary amino compounds, including aminoazo compounds and even 1-aminoanthraquinone derivatives[40]. Hitherto, phosgene had been the most widely used agent for linking two aminoazo compounds or amino-containing coupling components, such as J and γ acids, to form ureas. As already stated, it could not be used to form the ureas of the important 1:8-aminonaphtholsulphonic acids H, K, S, and 2S, owing to ring formation across the 1:8-positions, nor could it be used generally with one molecule each of two different amino or aminoazo compounds to form homogeneous mixed ureas. In addition to the latter, there were usually formed the symmetrical ureas from each of the two component amino compounds.

With cyanuric chloride, however, one chlorine atom can be replaced in the cold (0–20°C.), a second at 40–50°C., and the third at 90–100°C., and substantially homogeneous products are obtained. In practice the third chlorine is usually either left unreacted or treated with a colourless amine such as aniline, methylamine, or even ammonia. By condensing cyanuric chloride firstly with one molecule of an aminonaphtholsulphonic acid and then with one molecule of an aminoazo compound, coloured coupling components are built up. If azo dyes produced from such components contain an *oo'*-dihydroxyazo, *o*-hydroxy-*o'*-methoxyazo, or *o*-hydroxy-*o'*-carboxyazo residue, they can be converted into copper complexes with the usual increase in light fastness. If diamines such as *p*-phenylenediamine or 4:4'-diaminostilbene-2:2'-disulphonic acid are used as starting materials with two molecules of cyanuric chloride, one for each amino group, complex primary condensation products can be built up containing two triazine residues. By reaction of a further chlorine atom in each triazine residue with an aminoazo compound or with the amino group of an aminonaphthol derivative, in the latter case for subsequent coupling to diazo compounds under the directive influence of the hydroxyl group, and finally reaction of the two remaining chlorine atoms of the triazine residues with two molecules of aniline or other suitable amine, polyazo dyes containing two triazine residues can be synthesised. It will be apparent that the possibilities of variation in intermediate and dye structure based on this method of linking amino compounds are legion, and there is a vast patent literature on this theme.

One of the most important consequences of this discovery was the production of homogeneous green direct dyes by linking blue and yellow dye structures through amino substituents, the triazine residue providing a very effective "chromophoric block". Important cyanuric green dyes are—

CHLORANTINE FAST GREEN BLL (SCI)[41]
(= SIRIUS SUPRA GREEN BL (IG))



and fast-to-light yellowish-green ternary condensation products of cyanuric chloride with a blue 1-aminoanthraquinone derivative, a yellow aminoazobenzene derivative, and a base such as aniline[42]. Other commercial azo dyes based on the use of cyanuric chloride are—

CHLORANTINE FAST BLUE 8G (SCI)[43]

p-Nitroaniline-*o*-sulphonic acid→Cresidine→Secondary condensation product of 1 mol. each of cyanuric chloride, H acid, and *p*-aminoacetanilide

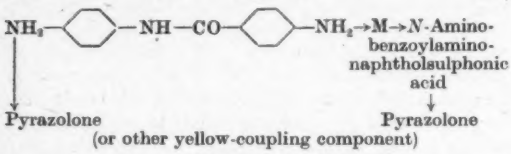
CHLORANTINE FAST RUBINE RLL (SCI)[43]

Bis-copper complex of the disazo compound obtained by coupling 2 mol. of 2-aminophenol-4-sulphonic acid with the ternary condensation product of 1 mol. of cyanuric chloride, 2 mol. of J acid, and 1 mol. of aniline

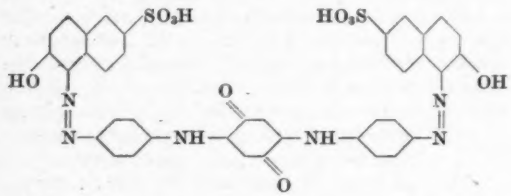
OTHER "CHROMOPHORIC BLOCKS"

Alternatives to cyanuric chloride have been proposed for linking amino-containing intermediates and colouring matters. Examples of these are 2:4-dichloroquinazoline, 1:4-dichlorophthalazine, and 2:4:6-trichloropyrimidine[44]. I.C.I. have used the benzoyl group as a "chromophoric block" for

building up greens from yellow and blue azo components[45]. In dyes of the type—



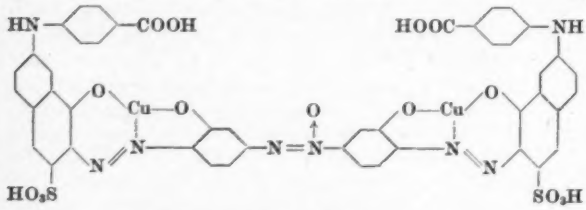
the central blue diaminodisazo structure is built up, and this on tetrazotisation and coupling to two molecules of a yellow-coupling component gives rise to a green-dyeing dye. I.G. have described the making of a mixed urea of the azo-anthraquinone series, giving greens on cotton, by condensing the *O*-phenylurethane of 4-amino-4′-hydroxy-3′-carboxyazobenzene with 1-amino-4-*p*-aminoanilinoanthraquinone-2-sulphonic acid[46] (with elimination of the phenoxy group of the urethane). A method of linking aminoazo dyes described by the Deutsche Hydrierwerke A.-G. consists in condensing them with quinones, e.g. chloranil, to give dyes of the type—



In this case the dye is said to be grey–violet in hue and of good fastness to acids and alkalis[47].

A further method of linking two molecules of a monoazo compound to form what is presumably a disazoazoxy dye should be mentioned. This consists in reducing a *p*-nitrobenzeneazonaphthol derivative under alkaline conditions, e.g. with glucose. Thus, glucose reduction of 5-nitro-2-anisidine→*N*-*p*-carboxyphenyl-γ acid followed by conversion of the reduction product to its bis-copper complex gives the fast-to-light bluish-grey dye of probable formula—

SIRIUS SUPRA GREY VGL (IG)[48]



STILBENE-AZO DYES

Considerable developments have taken place in recent years in the field of stilbene-azo dyes. New dyes have been patented based on caustic alkaline condensations of 4:4′-dinitrostilbene-2:2′-disulphonic acid with metallisable aminoazo compounds either alone or in admixture with one another or with various proportions of a non-metallisable amino or aminoazo compound. Examples of such metallisable aminoazo compounds[49] are—

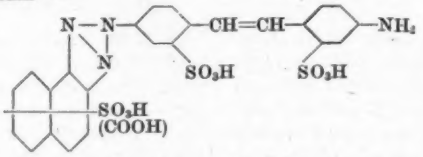
Anthranilic acid $\xrightarrow{\text{Alkali}}$ J acid

Anthranilic acid $\xrightarrow{\text{Alkali}}$ 2′-*m*-Aminophenyl-5-hydroxythiazolo(4′:5′-2:1)naphthalene-7-sulphonic acid

o-Aminophenols→*m*-Anisidine
(or their sulphonic or carboxylic acids)

o-Aminophenols→2:5-Dimethoxyaniline

Examples of non-azo amino compounds which have been described as components for such heterogeneous condensations are sulphonated or carboxylated aminodiaryltriazoles, e.g. 2-*p*-aminophenylnaphtho(1′:2′-4:5)triazole-5′:7′-disulphonic acid and 5-amino-2-*p*-sulphophenylbenzotriazole[50], and aminostilbene-naphthotriazoles of general formula[51]—



As a result, the former limited hue range of yellowish-orange to scarlet and reddish-brown dyes of good light fastness provided by condensations of 4:4′-dinitrostilbene-2:2′-disulphonic acid with non-copperable aminoazo compounds such as—

For SIRIUS SUPRA ORANGE 3R (IG)[52]
Sulphanilic acid→Cresidine

For SIRIUS SUPRA ORANGE 7G (IG)[53]
Sulphanilic acid→*m*-Toluidine

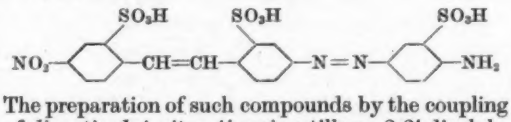
For SIRIUS SUPRA SCARLET 2G (IG)[54]
p-Anisidine-*o*-sulphonic acid→Cresidine

For SIRIUS SUPRA BROWN 3R (IG)[55]
Sulphanilic acid→α-Naphthylamine

has been extended to include many more dyes of brown hue, including deep browns, as well as greys and olives, good light fastness being maintained by utilising metallisable aminoazo reactants and converting the condensation products into their copper complexes. Solophenyl Brown RL and Grey 4GL (Gy) are probably examples of coppered dyes of this class. It should be remembered that variations in hue and fastness properties of these stilbene-azo condensation products can be effected by variations in the proportions of reactants and the strength of caustic alkali used, and in the duration and temperature of heating. Moreover, aftertreatments of the condensation products with reducing agents such as glucose and sodium sulphide and with oxidising agents such as sodium hypochlorite also effect variations in hue and fastness properties[56]. Thus, aftertreatment with reducing agents usually causes deepening (reddening) of the hue, whereas hypochlorite usually removes by-products of lower fastness, and has a hypsochromic and brightening effect on hue which is often accompanied by an increase in light fastness.

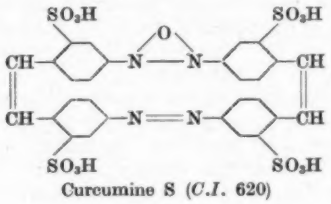
I.G. have claimed that homogeneous stilbene-azo dyes of very good discharge properties as well as good light fastness can be obtained by

stepwise condensation in caustic alkaline medium of 4:4′-dinitrostilbene-2:2′-disulphonic acid with *p*-phenylenediamine and its derivatives (1 mol. thereof, or 2 mol. of one diamine, or 1 mol. each of two different diamines) to give mono- or di-amino compounds[57]. These can be diazotised or tetrazotised, as the case may be, and coupled with a *para*-coupling phenol, the resulting product being alkylated to inhibit alkali sensitivity[58]. The primary condensation is carried out below 50°C., and the secondary at 80–85°C. This is said to be the only satisfactory process for the preparation of condensation products of 4:4′-dinitrostilbene-2:2′-disulphonic acid and sulphonic and carboxylic acids of *p*-phenylenediamine and their substitution products, e.g. for the preparation of the compound—



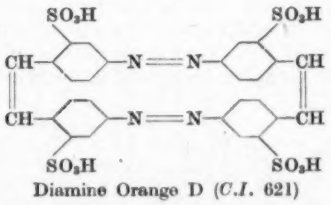
The preparation of such compounds by the coupling of diazotised 4-nitro-4′-aminostilbene-2:2′-disulphonic acid with *o*-aminobenzene-sulphonic or -carboxylic acids (for the above compound orthanilic acid would be required) is not feasible, since these acids couple with diazo compounds only very feebly, if at all[59].

Among the oldest stilbene-azo dyes are Curcumine S and Diamine Orange D (= Chloramine Orange G) (IG). The former is one of many brands of the mixtures of dyes obtained by the action of caustic alkali on *p*-nitrotoluene-*o*-sulphonic acid, and the latter, again one of many brands, is obtained by carrying out a similar reaction in the presence of reducing agents. The main constituents of these dyes were formulated by Green and Crossland[60] as follows—



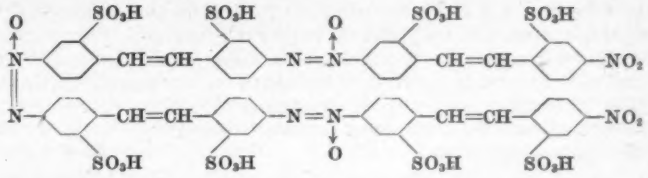
Curcumine S (*C.I.* 620)

Reduction

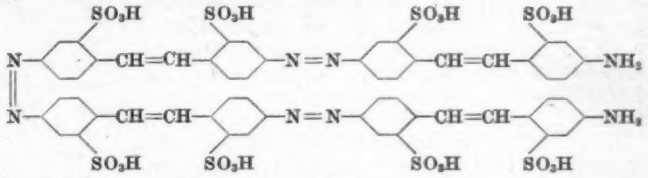


Diamine Orange D (*C.I.* 621)

The I.G. now consider that these formulations do not agree with the properties of these dyes. They have proposed for Curcumine S the new formula—



whilst they consider that Diamine Orange D is a mixture of Curcumine S of the above formula and its reduction product—



in which unreduced Curcumine is in excess. The amino groups of the diamino compound can be rendered innocuous by acylation, resulting in particularly valuable dyes[61].

Since 1931, 4-nitro-4′-aminostilbene-2:2′-disulphonic acid has been widely used as a starting material for stilbene-azo dyes. The I.G. were the first to use it for building up direct cotton dyes, but dyes based upon it have been patented also by S.C.I., Geigy, and I.C.I. It can be obtained by sodium sulphide reduction of 4:4′-dinitrostilbene-2:2′-disulphonic acid[62]. It has been submitted to the various reaction processes which are applicable to aminoazo compounds generally, e.g. phosgenation processes and reaction with cyanuric chloride, and formation of symmetrical and unsymmetrical polyazo dyes by diazotisation and coupling processes, with or without metallisation. In addition it has been treated with amines and aminoazo compounds in caustic alkaline media to give stilbene-azo compounds. Dyes of yellow, orange, brown, green, and grey hues derived from it have been described, among which may be mentioned the following commercial dyes of I.G. (A = 4-nitro-4′-aminostilbene-2:2′-disulphonic acid)—

Sirius Orange I[63]
Methylated (A→Phenol)

Sirius Supra Orange F3G[64]
Glucose reduction product of Sirius Orange I (a trisazo or disazo-azoxy dye)

Sirius Supra Olive GL[65]
Copper complex of—
Reduced Sirius Orange I→2-Ethoxy-1:6-Cleve acid→Acetyl-S acid

Sirius Supra Green BTL[66]
Copper complex of—
(A→Naphthionic acid) oxidised to triazole, nitro group reduced to amino→2-Ethoxy-1:6-Cleve acid→Phenyl-J acid

Green to greenish-grey dyeings of good light fastness are also given by copper complexes of the dyes[67]—
Reduced *N*-acyl-A→2-Alkoxy-Cleve acid→*N*-Acyl-J acid

Aminostilbene-triazoles of the type employed for Sirius Supra Green BTL have already been referred to as novel reactants used by I.C.I. for condensation

reactions with 4:4′-dinitrostilbene-2:2′-disulphonic acid in association with certain copperable aminomonoazo compounds to yield fast-to-light brown and olive dyes[68]. Geigy have described the preparation of copper-containing dyes yielding light-fast brown, olive, khaki, and grey hues by condensing monoazo compounds—

A→Salicylic acid or A→a Phenol (methylated)

with 4-aminoazobenzene derivatives containing metallisable groups in the *ortho* positions to the azo groups[69]. The 3-methyl-5-pyrazolone derivative prepared from A has been used by Ciba as starting point for a wide variety of coupling components for metallisable pyrazolone dyes. Its nitro group has been reduced to give the aminostilbene-pyrazolone, which, by reaction with phosgene or cyanuric chloride, has given bispyrazolone coupling components[70]. On the other hand, unsymmetrical double-coupling components have been obtained by reaction of one molecule of the aminopyrazolone with one molecule of phosgene and one molecule of an aminonaphtholsulphonic acid or with a primary condensation product of cyanuric chloride and an aminonaphtholsulphonic acid. Bispyrazolone coupling components have also been obtained by alkaline reduction of the nitropyrazolone to azoxy and azo derivatives with doubling of the parent molecule. The copper complexes of the azo dyes from these pyrazolone compounds and diazotised anthranilic acids and *o*-aminophenol derivatives are said to give yellows and browns of very good light fastness.

AFTERTREATMENT OF DIRECT COTTON DYES TO GIVE IMPROVED FASTNESS PROPERTIES

The past few years have witnessed considerable developments in the aftertreatment of direct cotton dyes on the fibre to give improved fastness properties and in the synthesis of dyes particularly responsive to such processes. By far the most important of these processes is that of coppering, which usually increases light fastness and, in many cases, fastness to wet treatments as well. Before the recent war the I.G. marketed a range of about ten dyes, for aftercoppering with copper sulphate, known as Benzo Fast Copper dyes. (The brand names of these were— Blue FBL, F3GL, and GL; Brown 3GL; Navy Blue BL; Red RL; Violet BBL; and Yellow BLN, GGL, and RLN.)[71] The I.G. continued to extend this range during the war by the marketing of eight further members (Bordeaux BL, Brown TL, Navy Blue RL and 3RL, Red GGL, Rubine RL, and Violet F3BL and 3RL) and the development of a further brown (Brown BRL)[71,72].

About 1938, Ciba entered this field with their Coprantine range and a new aftercoppering technique permitting one-bath processing by use of copper salts stable to weak alkalis, such as the salts of certain aliphatic hydroxycarboxylic acids, e.g. tartaric, lactic, and citric acids[73]. Salts for this purpose were marketed as Coprantine Salts 1 and 2. Geigy followed this lead with the introduction of their Cuprophenyl range in 1944. A further line of development was the marketing of certain cation-active substances to improve the washing fastness of direct dyes, typified by Fixanol C (ICI), Fibrofix (Courtaulds), Tinofix A (Gy), and Sandofix WE and LW (S). Such products, however, tend to diminish the light fastness of the original dyeing. These two lines of development merged in the Cuprofix range of Sandoz, since their recommended aftertreating agent (Cuprofix Salt) appears to be a mixture of a copper salt and a cationic organic nitrogenous dye-fixing substance.

Concurrently with the marketing of these ranges of aftercoppering dyes there has been intensive patenting campaigns designed to protect the manufacture of new dyes particularly suitable for such methods of application. The Swiss firms have been particularly active in this direction, and it would appear that they are making a strong bid to become the chief manufacturers of dyes for such aftertreatments.

The basic requirements for suitable azo structures to provide the most satisfactory fastness properties on aftercoppering would appear to be—

(*a*) The dyes must be substantive.

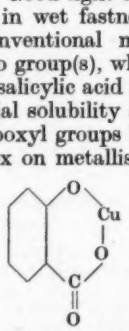
(*b*) They must be capable of application by the normal methods for direct dyes.

(*c*) They must contain groups capable of taking part in copper complex formation; i.e. their molecules should contain one or more *oo*′-dihydroxyazo, *o*-hydroxy-*o*′-carboxyazo, or *o*-hydroxy-*o*′-carboxymethoxyazo structures or an *o*-hydroxycarboxy grouping such as is found in salicylic acid and derivatives thereof. For the combination of good washing fastness with good light fastness, representatives of both types of groupings should be present.

(*d*) Their copper complexes should be insoluble or sparingly soluble in water.

(*e*) They should contain a minimum of sulpho groups consistent with structural requirements for desired hues.

It is obvious that the more the initial water-solubility of the parent dye can be made to depend on acidic groups, such as carboxyl, which are so positioned as to take part in true, alkali-stable, complex formation on metallisation, the greater is the likelihood of forming, on coppering, a sparingly soluble dye, and therefore one fast to wet treatments. Much of the recent patenting has been along these lines. Good light fastness and a considerable increase in wet fastness are secured by coppering the conventional metallisable groups adjacent to the azo group(s), whilst the incorporation, if desired, of salicylic acid residues provides a further aid to initial solubility and final good wet fastness, their carboxyl groups becoming involved in a stable complex on metallisation, thus—



and so no longer available for solubilising purposes.

It should be mentioned, however, that not all the dyes in the above commercial ranges give after-coppered dyeings whose light fastness properties are unaltered by washing treatments. This suggests that some of these dyes are structurally capable of forming only unstable copper complexes of the type formed by Chlorazol Sky Blue FF, such complexes gradually losing their initial improved light fastness under the influence of alkali with probable loss of copper. Moreover, some of the dyes of high light fastness have poor wet fastness, and *vice versa*. In a few cases, dischargeability would appear to be the distinctive property rather than fastness. Rarely are all these desirable properties combined in one dye.

Examples of dyes of the I.G. range are—

BENZO FAST COPPER YELLOW RLN[74]

1-*p*-Sulphophenyl-3-methyl-5-pyrazolone ←1— 4:4′-Diaminodiphenylurea-3:3′-dicarboxylic acid —2→ Acetoacetanilide

BENZO FAST COPPER RED RL[75]

6-Nitro-1-amino-2-naphthol-4-sulphonic acid → 1-*p*-Aminophenyl-3-methyl-5-pyrazolone phosgenated to the urea

BENZO FAST COPPER VIOLET BBL[76]

1-Naphthol-5-sulphonic acid ←1— Benzidine-3:3′-dicarboxylic acid —2→ Phenyl-J acid

BENZO FAST COPPER BLUE FBL[77]

p-Anisyl-J acid ←— Benzidine-3:3′-diglycollic acid → *p*-Anisyl-J acid

BENZO FAST COPPER BLUE F3GL[78]

5-Amino-2-hydroxybenzoic acid → 1-Amino-6-sulpho-2-naphthoxyacetic acid → *p*-Benzoylaminophenyl-J acid

BENZO FAST COPPER BROWN TL[79]

Phenylmethylpyrazolone ←1— Benzidine-3:3′-dicarboxylic acid —2→ 2:8-Dihydroxy-6-sulphonaphthalene-3-carboxylic acid

The good light and washing fastness properties of some of the Benzo Fast Copper dyes made them attractive substitutes for vat dyes under war conditions, and a good deal of work was done by the Germans during the war to extend their range, particularly in the direction of greys, browns, and greens[80]. The dye—

4-(4′-Aminobenzoylamino)benzeneazosalicylic acid —Acid 1→ H acid

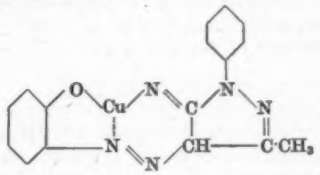
Pyridine 3 ↑

5-Aminosalicylic acid —2→ 1-Amino-6-sulpho-2-naphthoxyacetic acid

was said to be the best green obtained, an olive with light fastness 5–6 on aftercoppering. A new light-fast brown (said to be 7–8) which was fast to acid spotting (a deficiency of Benzo Fast Copper Brown TL) had the constitution—

Phenylmethylpyrazolone ←1— Benzidine-3:3′-dicarboxylic acid —2→ Bucherer condensation product from 2:8-dihydroxynaphthalene-6-sulphonic acid and 4:4′-diaminobenzanilide-3′-carboxylic acid

The I.G. found that the replacement of the keto group in 1-phenyl-3-methyl-5-pyrazolone by the imino group (1-phenyl-3-methyl-5-aminopyrazole) gave dyes which on aftercoppering were faster to light and washing and showed less change of hue on exposure to ammonia than corresponding dyes from phenylmethylpyrazolone. They considered the metal complex formed from a combination with a diazotised *o*-aminophenol to be of the type[81]—



The incorporation of salicylic acid residues in parent dyes for aftercoppering has been effected by using salicylic acid and its derivatives as coupling components and also by use of aminosalicylic acids as diazo components or reactants for cyanuric chloride condensation products. Thus, blue to green dyes which are said by S.C.I. to alter but little in hue on aftercoppering, but to acquire excellent fastness to light combined with very good washing fastness, are of the type[82]—

5-Amino-2-hydroxybenzoic acid → 2-Methoxy-1:6-Cleve acid → Ternary condensation product from 1 mol. each of (*a*) cyanuric chloride, (*b*) J, H, or K acid, (*c*) 4-amino-4′-hydroxy-3′-carboxyazobenzene, and (*d*) aniline

Green aftercoppered dyeings of even better wet fastness are said by S.C.I. to be obtained from parent dyes of the type[83]—

5-Amino-2-hydroxybenzoic acid → (*A*) *m*-Toluidine or cresidine → Ternary condensation product from 1 mol. each of (*a*) cyanuric chloride, (*b*) H, K, 2S, or S acid, (*c*) 4-amino-4′-hydroxy-3′-carboxyazobenzene, and (*d*) an amine such as aniline

It will be observed that the constitution of the example where cresidine is used as (*A*), (*b*) is H acid, and (*c*) and (*d*) are as exemplified above, differs from that of Chlorantine Fast Green BLL (p. 415) only in having 5-amino-2-hydroxybenzoic acid in place of H acid as the diazo component for the blue disazo residue. As an example of a dye containing four salicylic acid residues there may be mentioned the product obtained by condensing one molecule of 4:4′-diaminostilbene-2:2′-disulphonic acid with two molecules of cyanuric chloride and then replacing the remaining four chlorine atoms of the triazine residues by reaction with four molecules of 5-amino-2-hydroxybenzoic acid → cresidine[84]. According to S.C.I., the product dyes vegetable fibres yellow, the dyeings becoming very fast to washing on aftercoppering. The following combinations are examples of dyes which contain both an *oo*′-dihydroxyazo (or *o*-hydroxy-*o*′-carboxyazo) structure and a salicylic residue for coppering—

(i) 2-Aminophenol-4-sulphonamide → Ternary condensation product of cyanuric chloride, J acid, 4-amino-4′-hydroxy-3′-carboxyazobenzene, and aniline

(Reddish brown by one-bath aftercoppering process)[85]

(ii) 5-Amino-2-hydroxybenzoic acid→Cresidine→
di-J acid←5-Nitro-2-aminophenol

(Dyes cotton and viscose, with excellent exhaustion, in bright reddish blues, which become greener and considerably improved in light and wet fastness on aftercoppering)[86]

(iii) Salicylic acid←Benzidine→
1:3-Dihydroxynaphthalene←
4-Nitro-2-aminobenzoic acid

(Fast yellow–brown dyeings on cotton by the one- or two-bath aftercoppering process)[87]

Recently, Ciba Ltd. have taken out a considerable number of patents for dis- and tris-azo dyes derived from tetrazotised 3:3′-dihydroxybenzidine and coupling components which couple *ortho* to a hydroxyl group[88]. The objective here appears to be the production by aftercoppering of dyeings which otherwise could be obtained only by direct application of copper-containing dyes derived from dianisidine. Particular attention has been paid to blue disazo dyes from aminonaphthols and their sulpho derivatives and from certain dihydroxynaphthalenes (e.g. 2:6-, 2:7-, and 1:5-). Double coupling of the tetrazo compound cannot always be completely effected in sodium carbonate medium, particularly with J-acid and γ-acid derivatives and certain β-naphtholsulphonic acids. In such cases coupling is said to be satisfactorily carried out in a medium rendered alkaline with an alkali hydroxide (including ammonium hydroxide) or an alkaline-earth metal hydroxide[89]. The products obtained under these conditions of higher pH are said to be different from those formerly obtained under lower pH conditions[90]. When unsulphonated hydroxynaphthalenes or aminonaphthols which couple in a position *vicinal* to a hydroxyl group are used as coupling components, purer dyes and/or better yields are said to be obtained if the couplings are carried out in the presence of more than 25% of pyridine (calculated on the weight of the coupling mixture) than is the case when aqueous caustic alkali or aqueous pyridine solutions of much lower pyridine content are the media employed[90a]. 3-Hydroxybenzidine has been used with one molecule of a 3-alkyl-5-pyrazolone and one molecule of another coupling component, which may be an azo compound, for red aftercoppered dyeings fast to light and washing, e.g.[91]—

Salicylic acid←^{1}—3-Hydroxybenzidine—^{2}→1-*p*-Hydroxy-*m*-carboxyphenyl-3-methyl-5-pyrazolone

A wide variety of hues, including reds, has also been obtained by coppering dis- and tris-azo dyes from 3-hydroxy-3′-methoxybenzidine in substance or on the fibre. Thus, with two molecules of 1-*p*-hydroxy-*m*-carboxyphenyl-3-methyl-5-pyrazolone a dye is obtained which yields reds by the single-bath aftercoppering process, and with two molecules of S acid one which gives blue aftercoppered dyeings[92]. 4-Amino-4′-hydroxyazobenzene-3:3′-dicarboxylic acid also has been used as a diazo component for violet and blue dyes from J-acid derivatives[93]. Ureas obtained by phosgenating monoazo compounds of the type—

5-Amino-2-hydroxy-3-sulphobenzoic acid→Benzenoid amine

give orange dyeings on cotton and viscose which, on aftertreatment with copper formate and water-soluble bases of high molecular weight, become fuller and have good fastness to washing, water, and light[94]. Black aftercoppered dyeings have been obtained from dyes of the type[95]—

Salicylic acid←Diamine→J acid←$^{\text{Acid}}$—Anthranilic acid derivative

The above examples represent only a few of the large number of dye structures which have been patented by the three Swiss firms, Ciba, Geigy, and Sandoz, in this field of metallisable dyes.

DYES FOR AFTERTREATMENT WITH FORMALDEHYDE

Mention has already been made of the fact that the fastness to washing of certain direct dyes can be improved by aftertreatment with formaldehyde. There has been little expansion of the range of dyes available for this aftertreatment, but Du Pont have in recent years taken out a considerable number of patents for new polyazo dyes based on resorcinol as coupling component[96]. Generally speaking, resorcinol is not a good component for securing high light fastness, and it is likely that such dyes, even with good washing fastness on aftertreatment, would be unable to meet the competition of the Swiss and I.G. aftercoppering ranges in respect of light fastness. The I.G. have also given some attention to this class of dye in attempts to improve upon or extend their Benzoform range of formaldehyde-aftertreated dyes. Two new reds, a blue, and a brown in which they were interested have been reported[97]. The reds are—

2:4-Dihydroxybenzoic acid←4:4′-Diaminobenzanilide→
Phenyl-γ acid

(Good discharge properties)

Resorcinol←4:4′-Diaminobenzanilide→Acetyl-J acid

(Bright hue and good fastness properties)

The blue has the constitution—

Resorcinol←*p*-Phenylenediamine→1:6-Cleve acid→
1:6-Cleve acid→1-Naphthol-3-sulphonic acid

(Light fastness about 5)

whilst the brown is—

Resorcinol←4:4′-Diaminobenzanilide→Phenyl-γ acid

DYES FOR DIAZOTISATION AND DEVELOPMENT ON THE FIBRE

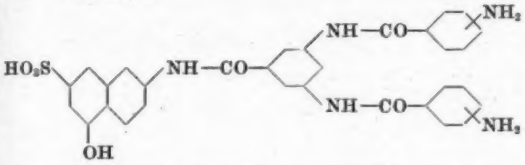
A steady flow of patents during the past twenty years for dyes for diazotisation (or tetrazotisation) on the fibre and development with coupling components devoid of solubilising groups can be recorded. Excellent dischargeability, better washing fastness, and extension of the hue range, particularly in blues and greens, appear to be the main objectives. Stress has been laid on good dischargeability under a variety of pH conditions. Many of these patents show that the introduction of *N*-aminoaroyl groups into suitable aminoazo dye structures continues to be one of the most facile ways of obtaining good affinity combined with ready diazotisability. *m*- and *p*-Aminobenzoyl derivatives of J acid have been more widely used as coupling components, and *m*- and *p*-aminobenzoyl derivatives of these have also been used. In the

latter case, if desired, the parent dye from *m*- or *p*-aminobenzoyl-J acid can be *m*- or *p*-nitrobenzoylated and the nitro group subsequently reduced.

Du Pont have found that on diazotising on the fibre disazo dyes of the type—

4-Aminoazobenzene-4′-sulphonic acid→ *N*-*m*-Amino-*p*-methoxybenzoyl-J acid

and developing with *β*-naphthol brighter hues are obtained than when the methoxy group is absent[98]. The same firm have also used 3:5-dinitrobenzoic acid as acylating agent for J acid: after reduction of the nitro groups to amino, the latter are acylated with *m*- or *p*-nitrobenzoyl chloride and the nitro groups reduced to give a coupling component of the type[99]—



I.G. have described a new Diazo red with excellent discharge properties, both neutral and alkaline, in[100]—

4-Aminodiphenyl-4′-carboxy-(*p*-hydroxy-*m*-carboxy)-anilide→*p*-Aminobenzoyl-J acid

whilst Du Pont have described disazo[101] and trisazo[102] dyes which yield fast-to-washing and dischargeable greens on development with phenylmethylpyrazolone, illustrated by the combinations—

Aniline→2-Methoxy-1:6-Cleve acid→*p*-Aminobenzoyl-S acid

Aniline-2:5-disulphonic acid→1:7-Cleve acid→ 2:5-Dimethoxyaniline→*p*-Aminobenzoyl-J acid

N-Aminoaroyl derivatives of 2-amino-6-naphthol-8-sulphonic acid have been used by Geigy as E in certain trisazo dyes—

A→M¹→M²→E

for blue–grey dyeings which on diazotisation and development with phenylmethylpyrazolone are said to yield fast yellowish-green colorations[103].

Brown dyeings of good dischargeability with neutral or alkaline discharging agents are said by I.G. to be obtained by tetrazotising on the fibre disazo dyes of the class[104]—

M or *γ* acid←3:3′-Diaminodiphenylurea→M, *γ*, or J acid

or by diazotising certain dyes of the class[105]—

A→M→Aminoaroylaminonaphthol-mono- or -disulphonic acid→Aminoarylpyrazolone

and developing with *m*-phenylenediamine or *β*-naphthol. *m*- and *p*-Aminobenzoyl derivatives of 4:4′-diaminodiphenylurea-3:3′-disulphonic acid have been used by I.G. as tetrazo components for coupling with 1-aminoaryl-5-pyrazolone-3-carboxylic acids or their esters to give disazo dyes which dye cotton yellow and give redder hues of yellow on tetrazotisation on the fibre and coupling with phenylmethylpyrazolone or orange hues with *β*-naphthol. Similar hue effects are obtained from monoazo dyes derived from diazotised *m*- and *p*-aminobenzoyl derivatives of dehydrothiotoluidinesulphonic acids and the same 1-aminoaryl-5-pyrazolone coupling components. The alkaline dischargeability of the developed dyeings in all these cases is said to be superior to that obtained with corresponding dyes from 1-aminophenyl-3-methyl-5-pyrazolones[106]. 2-Aminobenzidine has been used by Du Pont as end component (E) to provide the diazotisable amino groups for development in dyes typified by—

1-Sulphophenyl-3-methyl-5-pyrazolone←Benzidine→E

2-Naphthylamine-4:8-disulphonic acid→*m*-Toluidine→ *m*-Toluidine→E

which give orange–brown and maroon hues respectively on development with *β*-naphthol[107].

For a long time it was unknown to obtain yellows by employing *β*-naphthol as developer for ingrain dyes. In 1937 I.G. found that dyes of the type—

Salicylic acid←4:4′-Diaminobenzanilide→1-(3′-*p*-aminobenzoylaminophenyl)-5-pyrazolone-3-carboxylic acid

gave yellows with this developer[108]. Later work showed that if the above pyrazolone component was replaced by—

1-(3′-*p*-methylsulphonyl-*m*-aminobenzoylaminophenyl)-3-methyl-5-pyrazolone

pure yellows were obtained on development with *β*-naphthol[109].

Among new yellow-coupling developers which have been described are 5:6-dihydroresorcinol and similar enolisable hydroaromatic carbocyclic *β*-diketones. The fast-to-light greenish-yellow dyeings, which may be obtained, for example, by impregnating cotton with the bis-*p*-aminobenzoyl derivative of *p*-phenylenediaminesulphonic acid, tetrazotising on the fibre, and developing with 5:6-dihydroresorcinol, are said to be unobtainable by use of the usual yellow-coupling developers (e.g. phenylmethylpyrazolone or resorcinol) and to be superior in washing fastness to dyeings prepared with azo direct dyes of similar hue[110].

The use of compounds possessing both coupling positions and diazotisable amino groups, previously found serviceable in insoluble azo dye combinations of the azoic class[111], has been applied by I.G. to new dyes of the developing class primarily intended for the production of dyeings, fast to washing, on wool–viscose rayon unions. Such compounds are derivatives of J acid having an amino group in a position remote from the naphthalene nucleus, and they usually yield orange to red colorations on diazotisation and self-coupling. Examples are—*C*-*m*-aminophenyl-5-hydroxy-7-sulpho-1:2-naphth-iminazole, -thiazole, or -oxazole[112]; an aminobenzoylaminobenzoyl-J acid[113]; and certain 2-hydroxy-3-naphthoic arylamides such as the *p*-(*p*′-amino-*o*′-sulphoanilino)-*o*-toluidide[114], which gives navy blue hues. Red to blue–black monoazo self-coupling dyes of very good fastness, described by the General Aniline & Film Corpn., are obtained by coupling a diazotised 4-nitro- or 4-acylaminoaniline with certain naphthol- or chloronaphthol-sulphonyl derivatives of J acid or its *N*-methyl or

N-phenyl derivatives and reducing the nitro group or hydrolysing the acyl group[115].

A short series of dyes for producing fast blacks and blues on union materials of spun rayon and wool (e.g. the *ersatz* fibre Wollstra) has been developed by I.G. These dyes, known as Autazol Chrome dyes, contain diazotisable amino groups and, in some cases, an *oo'*-dihydroxyazo configuration as well which permits of metallising. The dyeing process appears to be carried out from a substantially neutral bath, after which the dyeing is submitted to treatment with nitrous acid, whereby the primary amino group (or groups) is (are) diazotised, the material then being given a treatment with ammonia and, finally, with a chromium salt. A special chroming composition, Autazol Chrome Salt R, is recommended for use with certain of the Autazol dyes. Examples of this range of dyes are[116]—

AUTAZOL CHROME BLACK R

5-Nitro-2-aminophenol $\xrightarrow{\text{Alkali}}$ J acid

AUTAZOL CHROME BLACK BA

1-Amino-5-naphthol-7-sulphonic acid → 1:7-Cleve acid $\xrightarrow{\text{Alkali}}$ γ acid

The author wishes to thank Messrs. Imperial Chemical Industries Ltd. (Dyestuffs Division), Blackley, Manchester, for permission to publish this paper.

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Discussion

Dr. H. E. NÜRSTEN: Some of the newer direct dyes may conceivably compete with and replace vat and azoic dyes on the one hand, and some of the old-established "bread-and-butter" direct dyes on the other. Have there been any noticeable trends in these directions?

Professor W. BRADLEY: How do the costs of some of the complicated newer commercial direct dyes compare with those of the older direct cotton, azoic, and vat dyes?

Mr. KNIGHT: There appears to have been, as yet, very little replacement of vats and azoics by even the best of the newer direct dyes, although on the cheaper furnishing fabrics direct dyes are used. The newer direct dyes are not particularly cheap, although, of course, they are easier to apply than vats or azoics. The costs of many of the more complicated new direct dyes, including some of the metallised dyes, are higher, in some cases much higher, than those of many of the old-established direct dyes. Many of the former dyes can be regarded as speciality products with limited outlets: nevertheless, the speciality product of to-day may become the "bread-and-butter" dye of to-morrow, and in this sense some replacement of old dyes is bound to occur, particularly as the general public is constantly pressing for, and learning to expect, higher fastness properties of the coloured materials which it buys.

WEST RIDING and SCOTTISH SECTIONS

Meetings held at the Great Northern Victoria Hotel, Bradford, on 26th January 1950, Mr. J. M. GOODALL in the chair; and at the St. Enoch Hotel, Glasgow, on 18th April 1950, Mr. D. B. F. MCANDREW in the chair

The Application of Logwood to Wool

C. L. BIRD and O. NEWSOME

The fastness properties of logwood on various metallic mordants have been studied, particular attention having been paid to fastness to light. The possibility of dyeing logwood blacks by a one-bath method based on the Bonsor process has been investigated in detail. Using a colorimetric method for the estimation of hæmatein, its rate of exhaustion on various mordants and the influence of the pH of the dyebath on the extent of exhaustion have been determined.

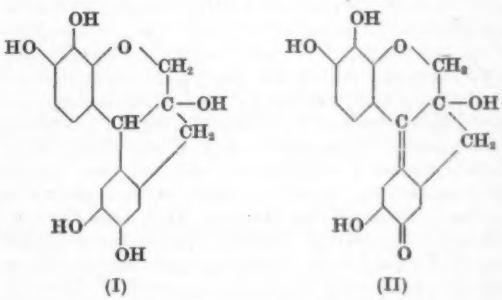
The fastness properties of fustic on chromium and iron–copper mordants, and the effect of fustic on the fastness properties of logwood blacks, have also been studied.

Introduction

Logwood is the heartwood of a large tree, *Hæmatoxylon campechianum*, which grows mainly in the West Indies. It was introduced into Europe by the Spaniards shortly after the discovery of America, and appears to have been first used in England during the reign of Queen Elizabeth, when its use as a dye was prohibited on the ground that it gave fugitive colours. It is presumed that this was due to the use of tin and aluminium mordants, which give purples and blues of poor fastness to light. Similar restrictions were placed on the use of logwood in other European countries, but the restrictions do not appear to have been rigidly enforced; and whether methods of application improved or standards of fastness declined, the use of logwood became general, and by the middle of the nineteenth century it was the most important of all dyestuffs.

The importance of logwood has declined somewhat in recent years, but it is still extensively used in the dyeing of blacks on wool, silk, and leather. It is also used for the dyeing of cellulose acetate rayon and nylon and has many other, minor uses. The present annual world consumption is approximately 30,000 tons.

The colouring principle of logwood is hæmatoxylin (I), which readily undergoes oxidation to hæmatein (II)—



(I) (II)

This oxidation is necessary before dyeing can occur, and may take place before or during the dyeing process.

The chemistry and properties of hæmatoxylin and hæmatein have been fully described by Perkin and Everest[1].

Logwood was formerly supplied to the dyer in the form of chips or powder, from which the colouring matter was extracted by boiling in the dyebath. Before use, the hæmatoxylin was partly oxidised to hæmatein by submitting the wood to an "ageing" process, which consisted in moistening with water and placing in heaps in a large airy chamber. The reaction was difficult to control, and if it was allowed to proceed too far a portion of the colouring matter was destroyed by further oxidation, the wood then being valueless as a dyeing material.

At the present time logwood is almost always used in the form of an extract, solid extracts being much more important than liquid extracts. The freshly cut wood is extracted with boiling water on the counter-current system, either in open pans (French method) or under pressure (American method). If desired, the hæmatoxylin may be partly or completely oxidised under controlled conditions. Finally, the extract is evaporated in vacuum pans, to a treacly consistency for logwood extract or to dryness for Hematine Crystals. The latter are well standardised products of known grades of oxidation, defined by the percentage of the total colouring matter which has been oxidised to hæmatein (Table I).

TABLE I

Commercial Brands of Hematine Crystals

Maker	Product— 98–100% oxidised	80–90% oxidised	15–20% oxidised
British Dyewood Co. Ltd.	Hematine Crystals S	Hematine Crystals A	Hematine Crystals B
West Indies Chemical Works Ltd.	Hematine Crystals ZA	Hematine Crystals C	Hematine Crystals NAD
Yorkshire Dyeware & Chemical Co. Ltd.	Hematine Crystals No. 1	Hematine Crystals No. 2	Logwood Crystals NAD

Subsequently in this paper the word *logwood* is used in a general sense, to indicate the colouring matter, which may be in the form of chipped wood or as a liquid or solid extract.

Logwood is a typical mordant dye, in that it produces only useless stains on wool in the absence of a metal with which it can form a co-ordination complex. The shade produced depends on the metal employed, and a large number of metals have been used in the past, those of greatest importance commercially being chromium, tin, aluminium, iron, and copper. Of these, only chromium is now used to any considerable extent in wool dyeing.

Mordanting is carried out by boiling the wool in a solution of sodium dichromate, with or without the addition of sulphuric acid ("oxidising" mordants), or with addition of acid reducing agents such as formic, lactic, or oxalic acid or cream of tartar ("reduced" mordants). It is usually considered that partly oxidised Hematine Crystals should be used on an oxidising mordant, oxidation then being completed at the expense of the mordant, while reduced mordants require fully oxidised Hematine Crystals. The work of Carlene, Rowe, and Speakman[2], however, suggests that there is less difference between the so-called oxidising and reduced mordants than was formerly thought. The following is a typical recipe which will illustrate the method of working—

The wool is entered at 50°C. into a bath containing 3% sodium dichromate on the weight of the material, and raised slowly to the boil. Boiling is continued for 1–1½ hr., and the wool is then thoroughly washed. Dyeing is carried out in a fresh bath with 8–10% Hematine Crystals C or ZA, starting at 50–60°C., raising to the boil in 20–30 min., and boiling for 1 hr. Where outstanding fastness to wet treatments is required an after-chroming with 0·25–0·5% dichromate is frequently given.

Dyeing on iron–copper mordant is carried out in a similar way, except that the mordant consists of 5% ferrous sulphate, 1–2% copper sulphate, and 3% oxalic acid or 7–10% cream of tartar. Iron blacks may also be dyed by the "stuffing and saddening" method. The wool is boiled for some time in a solution of Hematine Crystals; ferrous sulphate or a mixture of ferrous and copper sulphates is then added, and boiling is continued until the required shade is obtained. This method gives very dirty dyeings, but it is interesting to note that it is still in use in at least one dyehouse.

Several single-bath methods have also been used, the most successful of which was Bonsor's Black. In this method ferrous sulphate and copper sulphate are added to a logwood decoction, and the precipitated lake is dissolved in oxalic acid. Wool is then dyed by boiling in this solution. Chromium lakes have been used similarly, but were considered[3] to be less satisfactory than iron lakes. None of these single-bath methods is in use at the present time.

Logwood gives bluish blacks, and it is frequently necessary to modify the tone by addition of a yellow or orange dye. Old fustic, which is extracted from the wood of the tree *Chlorophora tinctoria*, growing in the West Indies, is the dye most commonly used, but synthetic chrome dyes are also used.

The main uses of logwood in wool dyeing are for loose wool, carbonised and uncarbonised rags, and wool hose. The properties which make logwood particularly suitable for these materials are—a rich bloomy shade, good covering power on kemps, burrs, and damaged fibres, lack of sensitivity to metals, and excellent fastness to alkaline milling. Its disadvantages are the two-bath process required and the fact that it is less fast to light than the best of the synthetic chrome blacks, the light-fastness figures being 6 and 7–8 respectively.

Most of the available literature on the application of logwood is very old. Further, owing to the absence in the past of standardised logwood extracts and of sound methods for assessing the fastness properties of dyed materials, it is often vague and contradictory, consisting largely of opinions unsupported by experimental evidence. This lack of reliable information seemed to justify a systematic investigation of the methods for applying logwood to wool, with the principal objects of obtaining improved methods of application and better fastness properties, and of deciding

by means of fastness tests points such as the correct amount of chrome mordant, which have been the subject of argument for many years. Complete success cannot be claimed, but many of the results which have been obtained are of practical importance, and others are of theoretical or historical interest.

Experimental

MATERIALS

Four kinds of wool material were used, viz. (1) a scoured unbleached flannel, (2) a scoured unbleached serge, (3) a white wool knitting yarn, described as yarn No. 1, and (4) a coarse wool carpet yarn, used only for dyeings for wet fastness tests. Small quantities of other wool materials were also used.

The brands of Hematine Crystals used were ZA, C, and NAD (see Table I). Small quantities of other brands of Hematine Crystals and of logwood chips were also used. Pure hæmatein was used for quantitative work, and was prepared from hæmatoxylin by the method of Engels, Perkin, and Robinson[4].

PROCEDURE

Dyeings were made in stainless steel beakers heated by gas in a Longclose revolving laboratory dyeing apparatus, using Leeds tap water (hardness 3°). Distilled water was used for quantitative work. Mordanting and dyeing were carried out in 40-vol. baths. The baths were prepared with the mordants and assistants at 40°C., the wetted-out patterns entered, and the baths raised to the boil in 30 min. After boiling for 1 hr. the patterns were thoroughly rinsed in water. With the YDC "Sequence" process[5], the patterns were entered at 40°C. into baths containing potassium dichromate only and raised to the boil in 30 min. After boiling for 10 min., sulphuric acid was added in three portions at 5-min. intervals, sodium thiosulphate then added, and boiling continued for 1 hr. longer. The mordanted patterns were entered into the dyebaths at 50°C., raised to the boil in 20 min., boiled for 1 hr., and then rinsed.

Hæmatein was estimated colorimetrically in exhaust dyebaths by means of the purple tin lake, using the following method— The solution to be tested was diluted to a concentration of 0·015 g. approx. hæmatein per litre. 10 ml. of this solution, and 10 ml. of a standard solution containing 0·015 g. hæmatein per litre, were placed in 100-ml. measuring flasks, and diluted to 90 ml. approx. with distilled water; 5·0 ml. of N. hydrochloric acid and 1·0 ml. of a 5% solution of stannous chloride in N. hydrochloric acid were added to each flask, and the contents diluted to 100 ml. After thorough mixing the solutions were compared in the Duboscq colorimeter, using the standard at a depth of 20 mm. Five readings were taken.

Details of the methods used in testing fastness properties are given in the Appendix.

Chrome Mordants

The work described in this section was mainly concerned with a study of the effect on fastness to light and wet treatments of variation in mordanting procedure. The effects of some aftertreatments and the properties of mixtures of logwood and synthetic chrome blacks were also studied.

FASTNESS TO LIGHT

Dyeings of 10% Hematine ZA were prepared on the following mordants—

3%	Potassium dichromate ("sweet" chrome)
2%	Potassium dichromate + 1% sulphuric acid
1·5%	Potassium dichromate + 1·5% formic acid (85%)
2%	Potassium dichromate + 1·5% oxalic acid
3%	Potassium dichromate + 6% tartaric acid
2%	Potassium dichromate + 2·5% sulphuric acid + 1·5% sodium thiosulphate ("Sequence" method)
2%	Potassium dichromate + 8% Mordant Acid H (British Dyewood Co.)*
3%	Potassium dichromate, reduced in a fresh bath with 5% sodium bisulphite

The dyeings were then tested for fastness to light. Dyeings of Hematine Crystals C and NAD on sweet chrome mordant were also exposed.

The differences in light-fastness produced by the different methods of mordanting were not large, except with the "Sequence" and Mordant Acid H methods, both of which were superior to the other mordants, the former being markedly so. Oxalic acid as a mordanting assistant gave a slightly lower fastness than the average.

The opinion that reduced mordants give better fastness to light than oxidising mordants is widely held and appears to be generally correct, but, with the exception of the cases mentioned, the differences are too small to be of practical importance. The partly oxidised Hematine Crystals C and NAD did not give better fastness on oxidising mordants than the fully oxidised ZA, but the shade of the ZA was slightly deadened by the oxidising mordant.

The fastness to light of Hematine on chrome mordants was found to be difficult to assess numerically, partly owing to the change of tone, and partly because the rate of fading increases with increasing time of exposure. An assessment made on a strongly faded pattern is thus much lower than one made on a slightly faded one, and when considering the effects of various treatments it was necessary to compare the treated patterns with untreated controls exposed at the same time.

It has been stated frequently[7–9] that an excess of chrome mordant reduces the fastness to light of logwood blacks, but with a series of dyeings of 10% Hematine ZA on sweet chrome and chrome–oxalic acid mordants in which the percentage of potassium dichromate was gradually increased from 1·0% to 5·0%, and on chrome–formic acid and "Sequence" mordants from 0·75% to 2·5%, fastness to light gradually increased to a maximum and then remained constant. Maximum fastness was obtained with 3·5% dichromate with sweet chrome, 2·5% with chrome–oxalic acid, and 1·25–1·5% with chrome–formic acid and "Sequence" mordants. Thus, there was no reduction in fastness with a 50% excess of chrome mordant, and the generally accepted view that an excess of chrome mordant

* Mordant Acid H is a mixture of acids designed to give complete exhaustion and reduction of the mordant[6].

reduces the fastness to light of logwood blacks appears to be disproved. Aftertreatment of a dyeing on chrome–oxalic acid mordant with 1% potassium dichromate was also without effect on fastness to light.

Addition of copper salts to chrome mordants or aftertreatment of dyeings with iron or copper salts has been considered[3,10] to improve the fastness to light of logwood, and therefore the effects of various metallic salts, as additions to the mordant bath and as aftertreatments, were examined. Dyeings were made with 10% Hematine ZA on a chrome–oxalic acid mordant with addition to the mordant bath of 1·5% of (*a*) ferrous sulphate, (*b*) copper sulphate, (*c*) ammonium molybdate, (*d*) potassium titanium oxalate, (*e*) nickel sulphate, and (*f*) potash alum. The effect of these additions on the fastness to light was negligible, except with iron and copper, which produced appreciable improvements, iron being the more effective. Aftertreatment with the same salts had similar but less marked effects.

The possibility of improving fastness to light by adding copper or iron to chrome mordants was then investigated in greater detail. Additions of 0·5%, 1·0%, and 1·5% copper sulphate were made to (*a*) sweet chrome, (*b*) chrome–formic acid, (*c*) "Sequence", (*d*) chrome–oxalic acid, and (*e*) chrome–tartar mordant baths. Hematine ZA on sweet chrome mordant with copper sulphate gave brownish blacks, but Hematine C gave normal shades. Normal blacks were obtained with Hematine ZA on reduced mordants with copper sulphate. This suggests that oxidation of the dye is catalysed by the presence of copper.

Addition of copper produced some improvement in light fastness with chrome–oxalic acid and chrome–tartar mordants and a marked improvement with chrome–formic acid, but was without effect on the "Sequence" mordant. The "Sequence" mordant, however, already possesses good fastness to light. The results with Hematine C on sweet chrome mordant were anomalous in that copper appeared to have no effect, but the dyeing without copper had unusually good fastness. 1·0% Copper sulphate was sufficient to produce the maximum effect. It thus appears that, while a useful improvement in fastness to light may be obtained by addition of copper sulphate to chrome mordants in some cases, it is not equally effective with all methods of mordanting.

The addition of iron salts to chrome mordant baths was found to present difficulties, since ferrous sulphate was oxidised by the dichromate, and hydrolysis of the ferric salt with precipitation of basic salts in the bath could not be prevented by practicable additions of sulphuric or formic acid. Precipitation could be largely prevented, however, by adding sufficient oxalic acid or cream of tartar, and additions of 0·5%, 1·0%, and 1·5% of ferrous sulphate were made to chrome–oxalic acid and chrome–tartar mordants, and to a mordant of 4% chromium fluoride + 2% oxalic acid. 1·0% Ferrous sulphate increased the fastness to light of dyeings on chrome–oxalic acid mordant from 6 to almost 7, but had no effect with chrome–tartar or chromium fluoride mordants. Ferric ammonium sulphate behaved in the same way as ferrous sulphate.

This method of improving fastness to light is not considered to be of practical importance, owing to the ease with which ferric salts are hydrolysed in the mordant bath, but a satisfactory method of combining iron and chrome mordants would probably be of interest.

Logwood blacks dyed on an indigo bottom were formerly considered to be much faster to light than ordinary logwood blacks, but patterns which were first dyed with indigo and then topped with Hematine on chrome mordants were only slightly faster than similar dyeings without indigo. Similarly, according to several authors[3,10] the characteristic green fade of logwood can be masked by shading with a fast red dye such as Alizarine Red, and this appears to have been common practice. Dyeings of 8% Hematine ZA, 2% Fustic Crystals No. 1 (YDC), and 1·0, 1·5, and 2·0% Alizarine Red AS (ICI) on sweet chrome and chrome–formic acid mordants showed no improvement in fastness, the fade being reddish instead of greenish. The method thus does not appear to be a very effective one, but the percentages of Alizarine Red AS used may have been excessive.

The fastness to light is affected by the depth of dyeing and falls off markedly with less than 8% of Hematine Crystals. It is considered that not less than 8%, and preferably 10%, of Hematine Crystals ZA should be used in dyeing logwood blacks on chrome mordants. Increasing the depth of Hematine ZA above 10% increases the fastness, but no large improvement of practical value is obtained.

It has been suggested[11] that the source and method of preparation of logwood extracts may affect fastness to light, and Knecht[10] appeared to be of the opinion that an artificially oxidised extract did not give the same fastness as the unprepared wood. It was found, however, that dyeings of pure hæmatein, various brands of Hematine Crystals prepared from Jamaican and Haitian woods by different methods, and aged logwood chips in equal depth were of equal fastness to light. It is therefore concluded that the fastness to light of a logwood black is independent of the method of preparation of the dye.

Logwood black on chrome mordant does not fade when exposed to light without access of air, and it is probable that fading is due to destruction of the colouring matter by oxidation. This suggests that the presence of substances which retard oxidation should also retard fading, but addition of natural or synthetic tannins to the dyebath or impregnation of the dyed material with β-naphthol or sodium thiosulphate had no effect on fastness to light.

The acidity of dyed patterns, as measured by the pH values of aqueous extracts, was found to increase on exposure. In order to determine whether the increased acidity was responsible for the increasing rate of fading, dyed patterns were neutralised and then impregnated with disodium hydrogen phosphate and sodium acetate respectively, and exposed to light. These patterns were

identical in fastness with those exposed in an acid condition, and it is concluded that fastness to light is not affected by the pH of the wool.

Calcium acetate and magnesium sulphate appear to have been used as additions to logwood dyebaths in the past, but the precise purpose of these assistants is not clear. Dyeings of 10% Hematine ZA were made on a chrome–tartaric acid mordant with addition of (*a*) 5% calcium acetate and (*b*) 5% magnesium sulphate to the dyebath. Calcium acetate increased the depth of shade and fastness to light very slightly, but magnesium sulphate was without effect on shade or fastness, and the additions appear to serve no useful purpose.

FASTNESS TO WET TREATMENTS

MILLING— Dyeings of Hematine ZA on a number of chrome mordants were tested and all were found to be of excellent fastness (5), apart from some dyeings on chrome–oxalic acid mordant. With this exception, fastness to milling does not appear to be seriously influenced by the method of mordanting. Addition of copper to the mordant did not affect the fastness appreciably.

POTTING— A large number of tests for fastness to potting were made, and this property was found to be somewhat sensitive to variation in mordanting procedure. The fastness of dyeings on different chrome mordants varied from moderate (3–4) to very good (4–5), the best results being obtained with Mordant Acid H, chrome–formic acid, and "Sequence" methods, in that order. Aftertreatment of the dyed wool with potassium dichromate increased the fastness to 5. Increasing the percentage of potassium dichromate from 1·0 to 5·0 with sweet chrome mordant, and from 0·75 to 2·5 with chrome–formic acid and "Sequence" mordants, gave a progressive increase in fastness. The highest fastness obtained, however, was 4–5, and the staining on the undyed wool appeared to be due to unfixed Hematine. It thus appears that even when an excess of chrome mordant is present a portion of the absorbed dye remains uncombined with the mordant and requires to be fixed by afterchroming. The presence of traces of residual oxalic or tartaric acid in the dyed wool reduced fastness to potting appreciably.

SULPHURIC ACID CROSS-DYEING— A number of dyeings were tested, and the results were mostly poor, the best fastness of 3–4 being obtained by the Mordant Acid H method, thus confirming the well known lack of fastness of logwood blacks to acid treatments.

PERSPIRATION— Dyeings of 10% Hematine ZA on sweet chrome, chrome–formic acid, and "Sequence" mordants were tested, and all gave excellent fastness (5).

ALKALI (STREET MUD)— All the dyeings submitted to this test gave excellent fastness (4–5 to 5), except those on chrome–oxalic acid mordant, which were somewhat inferior.

ACID SPOTTING— When spotted with hydrochloric acid, all the dyeings changed shade more or less, but spotting with acetic acid had little or no effect.

Mixtures of Hematine and Synthetic Chrome Blacks

There are several references in the literature[12–14] to the dyeing of fast-to-light blacks with mixtures of Hematine and synthetic chrome blacks, and some experiments were carried out in this connection. A series of dyeings was made with 5% Hematine Crystals ZA and 5% of various synthetic chrome blacks on a chrome–formic acid mordant, the dyeings being tested for fastness to light and milling (Table II).

TABLE II

Fastness to Light and Milling of Hematine–Chrome Black Mixtures
(5% Hematine ZA + 5% Chrome Black)

Chrome Black	Light	Milling— Change of Shade	Milling— Staining of Wool
Durochrome Black A (YDC) ...	6	4	4
Durochrome Black T (YDC) ...	7–6	4	4
Solochrome Black WDFA (ICI) ...	7–6	3–4	3–4
Solochrome Black FS (ICI) ...	7	3–4	3–4
Solochrome Black PGS (ICI) ...	6	3–4	3
Eriochrome Black X (Gy)	7	4	3

For general fastness properties the mixture with Durochrome Black T appeared to be the most suitable, and light-fastness tests were made on a series of dyeings with different proportions of Hematine ZA and Durochrome Black T (Table III). The dyeing containing 4% of each dye gave a fastness figure of 7, and it is considered that a mixture of this type requires 4% of the Black T to give maximum advantage.

TABLE III

Fastness to Light of Hematine–Chrome Black T Mixtures

Hematine ZA (%)	7	6	5	4	3	2	1
Durochrome Black T (%)...	1	2	3	4	5	6	7
Fastness to light	5	6	6–7	7	7	7–8	7–8

It is well known that synthetic chrome blacks do not give maximum fastness to wet treatments when dyed on chrome mordants, and the fastness of the mixtures to milling (3–4), as shown in Table II, was not satisfactory. The lack of fastness is probably due to incomplete combination of dye and mordant, and the effect of afterchroming was tried. Dyeings of 5% Hematine ZA and 4% Durochrome Black T on a chrome–formic acid mordant were boiled for 30 min. with 0·25, 0·5, 0·75, and 1·0% potassium dichromate, and tested for fastness to light, milling, and potting (Table IV).

TABLE IV

Effect of Afterchroming on the Fastness of Hematine–Chrome Black T Mixtures

Potassium Dichromate (%)	Light	Milling— Change of Shade	Milling— Staining of Wool	Potting— Change of Shade	Potting— Staining of Wool
0	7	4	4	3	2
0·25	7	4–5	4–5	4–5	3
0·5	7	4–5	5–4	5	4
0·75	7	5–4	5–4	5	4
1·0	7	5	5	5	4–5

Fastness to light was unaffected by afterchroming, but there was a marked increase in fastness to milling and potting with 0·25% potassium dichromate, and a further gradual increase up to 1·0%.

Blacks of this type may also be dyed by applying the chrome black by the usual afterchrome method and then topping with logwood. This method was

compared with the chrome mordant method, and the results of fastness tests are shown in Table V. The synthetic chrome blacks were chromed in the exhausted dyebath with 2% potassium dichromate for 45 min. at the boil, and topping with Hematine ZA was carried out in a fresh bath for 1 hr. at the boil.

TABLE V

Fastness of Hematine–Chrome Black Mixtures and Chrome Blacks topped with Hematine

Dyeing Method	Light— 309 hr.	Light— 508 hr.	Milling— Change of Shade	Milling— Staining of Wool	Milling— Staining of Cotton
CHROME–FORMIC ACID MORDANT					
8% ZA	6	4–5	5–4	5	5
*4% ZA + 4% Durochrome Black T	–	7	5	5	5
*4% ZA + 4% Solochrome Black PVS	6–7	6–5	5–4	5	5
CHROME–MORDANT ACID H					
8% ZA	6	4–5	5	5	5
*4% ZA + 4% Durochrome Black T	–	7–8	5	5	5
*4% ZA + 4% Solochrome Black PVS	7	6	5–4	5	5
AFTERCHROME					
8% Durochrome Black T	–	7–8	5	4–5	5
8% Solochrome Black PVS	6	6	5	5	5
4% Black T, topped 4% ZA	–	7	5	5	5
4% Black PVS, topped 4% ZA	6–7	5–6	5	5	5

* Afterchromed with 1% potassium dichromate

All these dyeings were of satisfactory fastness to milling, but mixtures with Black PVS were inferior in fastness to light to those with Black T. The figures for the first exposure indicate that 50 : 50 mixtures of Hematine ZA and Black PVS have better fastness to light than either dye alone, a result which may be due to the Hematine fading greener and the Black PVS redder, the two fades tending to neutralise each other in the earlier stages of fading. It appears to be immaterial whether the chrome black is dyed by the afterchrome method and topped with logwood, or whether the two dyes are applied simultaneously on mordanted wool, provided that, in the latter case, the dyeing is afterchromed.

Dyeing in admixture with a suitable chrome black appears to be the only method by which a large improvement in the fastness to light of logwood blacks on chrome mordants may be obtained. The process is a long one, but the mixture covers kemps and burrs better than the synthetic chrome blacks and is superior in shade, while it is much faster to light than logwood, a combination of properties which apparently cannot be obtained in any other way.

Single-bath Methods

Although several single-bath methods for dyeing logwood blacks have been used in the past, none has survived. From such information as could be obtained from the literature[3,10,15,16], Bonsor's Black appears to have been the most widely used and the most satisfactory of the single-bath methods, and, as it was reputed to be of good fastness to light, the possibility of devising a suitable method based on the Bonsor process was investigated in detail. Some experiments were also made on the dyeing of single-bath logwood blacks with a chrome mordant, and the results are summarised briefly at the end of this section.

SINGLE-BATH IRON–COPPER BLACKS

The method of working was to add a solution of Hematine ZA to the dyebath, followed by solutions of ferrous sulphate, copper sulphate, and oxalic acid. The wetted-out patterns were entered at 40°C., raised to the boil in 30 min., and boiled for 1 hr. They were then rinsed in cold water, treated with dilute sodium carbonate solution to neutralise excess oxalic acid, and again rinsed.

Blacks of satisfactory shade and fastness to light and milling were obtained, but fastness to rubbing was poor, so the effect of adding dispersing agents of different types was tried. Additions of 0·25, 0·5, 1·0, 2·0, and 4·0 g., per litre, of (*a*) Dyapol T (YDC), (*b*) Dispersol A (ICI), (*c*) Nekal BX dry (IG), and (*d*) Teepol (Shell), were made to the dyebath, and the dyeings were tested for fastness to rubbing. Only Dyapol T gave improved fastness; it was effective in a concentration of 1 g. per litre.

Experiments were made in which the concentration of each component of the dyebath, temperature, duration of dyeing, and liquor ratio were varied in turn, and it was established that 5% ferrous sulphate was required to give the maximum depth of shade and fastness to light, and that 4% oxalic acid was necessary to maintain the dye lake in solution throughout the dyeing process. The percentage of copper sulphate could be varied from 1·0 to 2·25 without appreciable effect on shade or fastness, but a full black could not be obtained with ferrous sulphate alone. Copper sulphate did not form a lake in presence of oxalic acid, and gave only orange–brown shades.

The following recipe was finally adopted—

10%	...	Hematine Crystals ZA
5%	...	Ferrous sulphate
2%	...	Copper sulphate
4%	...	Oxalic acid
1 g./litre		Dyapol T.

Dyeings were made in 30-vol. baths, starting at 40°C., raising to the boil in 30 min., and boiling for 1 hr. The patterns were then rinsed in cold water, treated in 0·2% sodium carbonate solution for 20 min. at 50°C., and again rinsed.

Blacks dyed on flannel by this method were of very good fastness to light (6–7), excellent fastness to milling (5), and very good fastness to potting (4–5 to 5). Fastness to rubbing was also good.

Replacing the ferrous sulphate with pyrolignite of iron, and the copper sulphate with copper acetate or lactate, was of no advantage. Other solvents for the dye lake were tried in place of oxalic acid, viz. Trilons A and B (IG), formic acid, and tartaric acid, but satisfactory dyeings could not be obtained. Partial replacement of the oxalic acid by sulphuric or formic acid was also tried, but an addition of at least 3% of oxalic acid was necessary to maintain the lake in solution.

The above recipe gave full blacks on flannel, serge, a shoddy cloth, carpet yarn, and two samples of knitting yarn, but only thin blue–blacks on yarn No. 1 (p. 425). A slight increase in the depth of shade on yarn No. 1 was produced by increasing

the percentage of Hematine, or boiling for a longer period in the dyebath, but a full black could not be obtained by any variation of the recipe.

The rest of the work described in this section was concerned with a study of the causes of the poor shades obtained on yarn No. 1, and an attempt to make the method applicable to all kinds of wool.

It has been stated frequently[3,10,15] that the acidity of the Bonsor dyebath increases with increasing time of dyeing, and that more complete exhaustion may be obtained by partial neutralisation of the bath with sodium carbonate after dyeing for some time. The pH changes in the single-bath iron–copper black dyebath, and the possibility of obtaining fuller shades on yarn No. 1 by partial neutralisation, were investigated.

Dyeings were made on patterns of flannel, and after raising to the boil in 30 min. the pH values of the baths were measured at intervals (Table VI), after first cooling to 18°C.

TABLE VI
pH Changes in Single-bath Iron–Copper Black Dyeings
(Initial pH = 1·96)

Time of boiling, hr....	0	0·25	0·5	1·0	1·5	2·0
pH	2·70	2·73	2·74	2·75	2·76	2·77

It is seen that the pH, which is initially 2·0, rises rapidly to 2·70 and then increases very slightly. There is no indication of an increase in acidity, and the statements quoted appear to be disproved.

Dyeings were also carried out on flannel and on yarn No. 1 with (*a*) no extra addition, (*b*) addition of 1% sodium carbonate after boiling for 30 min., and (*c*) addition of 1% sodium carbonate after boiling for 30 min. and a further 1% after boiling for 45 min. The initial and final pH values were measured after cooling to 19·5°c., the results being given in Table VII.

TABLE VII
Effect of adding Sodium Carbonate on the pH of Single-bath Iron–Copper Black Dyeings

Addition to Dyebath	pH— Initial	pH— Final— Flannel	pH— Final— Yarn No. 1
None	2·0	2·78	2·80
1% Sodium carbonate	2·0	3·04	3·05
2% Sodium carbonate	2·0	3·44	3·47

Addition of sodium carbonate gave fuller shades on the flannel but not on the yarn. The second addition of sodium carbonate caused slight precipitation in the dyebath, and it seems probable that the pH should not exceed 3·0; above this value precipitation occurs owing to a lack of sufficient oxalic acid to keep the dye lake in solution.

It was at first thought that yarn No. 1 contained fibres which, owing to some form of damage, had a reduced capacity for absorbing Hematine or mordants, but dyeings on patterns of flannel which had undergone chemical modification as a result of (*a*) hydrogen peroxide bleaching, (*b*) carbonising, (*c*) chlorination, (*d*) treatment with alkali, and (*e*) sulphur stoving all gave fuller blacks than the untreated material, and a Pauly test on the yarn showed that it was substantially free from damaged fibres.

The quantities of iron absorbed by yarn No. 1 and flannel from baths containing 5% ferrous sulphate, 2% copper sulphate, and 2·0–6·5% oxalic acid were determined by analysis of the residual baths, and were found to be practically identical. The percentage exhaustion of baths containing Hematine and oxalic acid in the presence and absence of mordants by yarn No. 1 and a worsted yarn on which a full black was obtainable was also determined, the results being given in Table VIII.

TABLE VIII
Absorption of Hematine by Wool Yarns in Presence and Absence of Mordants

Dyebath	Exhaustion (%)— Yarn No. 1	Exhaustion (%)— Worsted Yarn
10% Hematine ZA + 4% oxalic acid...	32	33
Single-bath iron–copper black ...	60	61

Although slightly more Hematine was absorbed by the worsted yarn than by yarn No. 1, the difference was insufficient to account for the difference in shade. This led to the conclusion that the thin shades on yarn No. 1 must be the result of an optical effect—a conclusion that was confirmed by microscopic examination. In materials which gave a full black by the single-bath method, all the fibres were heavily dyed, but undyed and partly dyed fibres were present in yarn No. 1. Dyeings on yarn No. 1 by methods which gave a full black, e.g. Hematine on chrome mordant, did not contain undyed fibres. It was therefore concluded that the thin shades on yarn No. 1 were due to skittery dyeing or "fibre-selectivity", and experiments were made to determine the cause of the skitteriness.

Dyeings were made on a wool waste which was expected to give skittery results, with (*a*) Durochrome Black T (YDC), (*b*) Hematine ZA on chrome–formic acid mordant, (*c*) single-bath iron–copper black, and (*d*) a modified single-bath method in which the wool was boiled for 1 hr. with the mordants and oxalic acid before addition of Hematine and Dyapol T. Full and fairly solid blacks were obtained by all the methods except (*c*), which gave a mixture of black and brown fibres. The black and brown fibres were separated and tested for the presence of iron and copper. The black fibres contained both iron and copper, but the brown fibres contained only copper, which does not form a lake with Hematine in presence of oxalic acid; all the fibres contained Hematine. The skitteriness of the single-bath black thus appears to be due to the selective absorption of iron, which must be caused by the presence of Hematine in the dyebath, since premordanting gives more solid dyeings.

In a further series of experiments yarn No. 1 was boiled with ferrous sulphate, copper sulphate, and oxalic acid for periods varying up to 1 hr. before adding Hematine and Dyapol T. The depth and solidity of the shade increased with increasing time of boiling before adding Hematine, boiling for 1 hr. giving a fairly full and uniform black. It is concluded that, while the single-bath method is liable to give skittery dyeings, premordanting gives reasonably solid shades, and methods which are intermediate between the two give corresponding degrees of skitteriness.

Some observations during previous experiments had suggested that Dyapol T might increase the

degree of skitteriness, and single-bath dyeings were made on yarn No. 1 with and without addition of 1 g. Dyapol T per litre. The dyeing without Dyapol T was somewhat skittery, but less so than that with addition of Dyapol T. Addition of Dyapol T to the iron–copper mordant when dyeing by the two-bath method also caused the dyeing to be skittery. The effect of Dyapol T in increasing skitteriness is unfortunate in view of the fact that it is the only dispersing agent known to be effective in improving fastness to rubbing.

The impurities in commercial Hematine Crystals consist partly of tannins or closely related substances, and it was thought that these might have some effect on the skitteriness of the single-bath dyeings. Dyeings were therefore made on yarn No. 1 with equivalent quantities of Hematine ZA and pure hæmatein, and of pure hæmatein with addition of (*a*) 5% mimosa extract, (*b*) 5% sumac extract, (*c*) 5% tannic acid, (*d*) 2% Fustic Crystals No. 1 (YDC), and (*e*) 1 g. Dyapol T per litre. The dyeing with pure hæmatein was fuller than that with Hematine ZA, and microscopic examination showed it to be much less skittery. The dyeing was made much more skittery by addition of tannic acid, and somewhat more skittery by sumac extract and Dyapol T; mimosa extract and fustic were practically without effect. It is concluded that the inherently skittery nature of the single-bath black is accentuated by the presence of tannins in Hematine Crystals. Previous observations on the action of Dyapol T in increasing skitteriness are confirmed.

A number of auxiliary products which are claimed to prevent skittery dyeing with acid dyes and chrome dyes were tried as additions to the single-bath iron–copper black. The following products were used in concentrations recommended by the respective manufacturers—(*a*) Tipsols LR and MB (Gardinol Co.), (*b*) Calcomet Salt (American Cyanamid Co.), (*c*) X-tip (Drew), (*d*) Cystol W (Gy), (*e*) Peregal TW (General Dyestuffs), and (*f*) Anthomine (Arkansas Co.). None of the products produced any improvement in skitteriness, and all caused the shades to rub badly.

The tendency of the single-bath iron–copper black to give skittery dyeings appears to be an insuperable problem, although it can be partly overcome by mordanting with iron, copper, and oxalic acid, and then dyeing in the exhaust mordant bath. This method was tried on a bulk scale with a batch of 300 lb. of wool in a Simplex machine, but, although a satisfactory black was obtained, the dyeing was dirty and required extra washing. This is thought to be due to the poor exhaustion of the dyebath (60–65%), the dye lake contained in the liquor retained by the wool being precipitated on dilution by the wash water and then filtered out by the wool.

SINGLE-BATH CHROME BLACKS

In dyeing with logwood in the presence of metachrome mordant or of mixtures of potassium chromate and ammonium oxalate, a lake was rapidly formed in the dyebath and only thin grey shades were obtained. Dyeing with 10% of Hematine ZA or C in the presence of potassium dichromate and oxalic acid gave thin greyish blacks, whilst Hematine NAD gave a fairly full black. An addition of 1% copper sulphate gave a clearer bath and a fuller shade in all cases. Somewhat better results were obtained when the chromium was in the form of chromium oxalate, and addition of copper sulphate was again found to be advantageous, the best results being obtained with 10% Hematine ZA, 2·5% chromium oxalate, 1·25% oxalic acid, and 1·0% copper sulphate.

Chromosol Mordant (S) was found to be better than chromium oxalate, and a fairly full blue–black was obtained by dyeing with 10% Hematine ZA, 6% Chromosol Mordant, and 1·0–1·2% oxalic acid. Addition of oxalic acid was found to be necessary with both chromium oxalate and Chromosol mordant to prevent precipitation of the dye lake in the bath.

These experiments were carried out on flannel, and further dyeings were made on yarn No. 1 and wool waste. These dyeings showed the single-bath chrome black to be even more skittery than the iron–copper black. The shades were thin and contained black and brown fibres; the brown fibres contained Hematine, but only a trace of chromium was present. Dyeings on wool which had been previously mordanted with Chromosol mordant were satisfactory, and, as with the iron–copper black, the skitteriness appears to be due to selective absorption of the mordant, caused by the presence of Hematine in the dyebath.

An attempt was also made to dye Hematine by the Calcomet process[17], but the lake was formed in the dyebath and only thin grey shades resulted.

None of the single-bath chrome blacks obtained with Hematine had satisfactory fastness properties, and they do not appear to be of practical interest.

Iron, Copper, and Iron–Copper Mordants

Iron and iron–copper mordants were formerly of great importance in logwood dyeing, but they have now been almost completely superseded by chrome mordants. The shortage of chromium compounds resulting from the 1939–45 war, however, caused some revival of interest in iron mordants, and they were studied in more detail than their present limited use might appear to warrant.

Mordanting with iron and copper is usually carried out with 5% ferrous sulphate, 1–2% copper sulphate, and 2–3% oxalic acid or 7–10% cream of tartar. Both assistants were found to give good results, but cream of tartar was somewhat better than oxalic acid. In mordanting with iron without copper, however, oxalic acid gave better results than cream of tartar. Dyeings of 10% Hematine ZA on a mordant of 5% ferrous sulphate, 1·5% copper sulphate, and 10% cream of tartar gave the highest figure for fastness to light (7) of all the Hematine dyeings examined; fastness to milling was excellent (5) and fastness to potting very good (4–5). There was no advantage in increasing the percentage of ferrous sulphate to 10%.

It was formerly considered that fuller shades were obtained if iron-mordanted wool was allowed to lie exposed to air overnight before dyeing, the

effect being ascribed[10] to oxidation of the mordant from the ferrous to the ferric state. Oxidation of the mordant on the fibre by means of nitrous acid or hydrogen peroxide, however, was not found to improve either the shade or the fastness to light when dyeing with Hematine ZA.

A further series of dyeings was made with 10% Hematine ZA on a mordant of 5% ferrous sulphate and 3% oxalic acid without further addition, and with addition to the mordant bath of (*a*) 2% copper sulphate, (*b*) 2% copper sulphate and 2% potash alum, (*c*) 2% titanium potassium oxalate, (*d*) 2% ammonium molybdate, (*e*) 2% sodium tungstate, (*f*) 2% nickel sulphate, (*g*) 2% potash alum, and (*h*) 2% stannous chloride. Fastness to light was reduced by addition of nickel, tin, aluminium, or titanium, while copper, tungsten, and molybdenum were practically without effect. This result is surprising in view of the fact that copper has usually been considered to improve the fastness to light of logwood on iron mordants.

The observation that copper does not increase the fastness to light of dyeings on iron mordant raises the question of the function of copper in the usual iron–copper mordant. It was observed that, although iron–oxalic acid mordant baths had a tendency to form a yellowish-white precipitate (presumably ferrous oxalate), precipitation did not occur in presence of copper, and its use is probably justified for this reason. It was also found that a satisfactory iron mordant could not be obtained with cream of tartar as assistant unless copper was present. Some further dyeings were made on patterns mordanted with copper sulphate and oxalic acid, but only orange–brown shades were obtained, which were changed to blue–black by treatment with alkali. It thus appears that the H matine–copper lake cannot be formed in the presence of even small amounts of oxalic acid. Patterns mordanted with copper sulphate and tartaric acid dyed black normally, but gradually became browner when boiling in the dyebath was prolonged, indicating some decomposition of the lake. By dyeing copper-mordanted material with 2% Hematine ZA, it was found that a blue lake was formed at low temperatures, but that this gradually changed to drab on boiling. This was thought to be due to oxidation of the colouring matter by excess copper sulphate, but the change was not prevented by using unoxidised Hematine or by adding reducing agents to the dyebath. Copper does not appear to behave in this way when iron is also present. The precise function of the copper is thus not by any means clear, but its use appears to be beneficial with iron–oxalic acid, and necessary with iron–tartar, mordant.

Experiments were made to determine whether oxalic acid and cream of tartar could be replaced by other acids, viz. sulphuric, formic, lactic, phosphoric, salicylic, phthalic, or anthranilic acid, or sodium bifluoride. Satisfactory mordanting and dyeing could not be obtained with any of these acids as mordanting assistants. The specific action of oxalic acid and cream of tartar in mordanting, and the fact that they cannot be replaced by other acids, does not appear to have been sufficiently appreciated. It seems probable that their effectiveness is due to their ability to form stable co-ordination complexes which contain the metal in the anion.

The effect of varying the concentration of oxalic acid in the mordant bath on the absorption of iron by wool flannel was determined by colorimetric estimation of the iron in the residual baths, using thioglycollic acid. Baths containing ferrous sulphate and oxalic acid were first tried, but precipitates were formed during mordanting when more than 3% oxalic acid was present, and reproducible results could not be obtained. Copper was found to prevent precipitation, and the absorption of iron from baths containing 5% ferrous sulphate, 2% copper sulphate, and 2·0–6·5% oxalic acid was determined. The results are illustrated by Fig. 1.

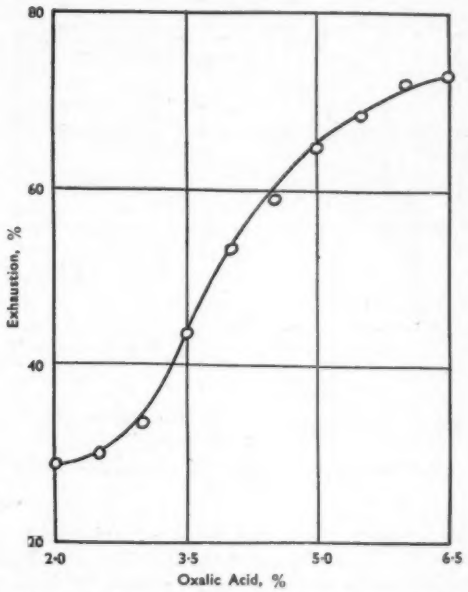


FIG. 1—The Absorption of Iron by Wool in presence of Oxalic Acid

The absorption of iron increased with increasing percentage of oxalic acid, and appeared to be approaching a maximum with 6·5%, which is equivalent to 1·99 molecules of oxalic acid per atom of mordanting metal. The action of oxalic acid is thus in sharp contrast to that of other acids, e.g. sulphuric acid, which reduce the absorption of mordanting metals[18]. It is significant that maximum absorption occurs with approximately two molecules of oxalic acid per atom of mordanting metal, since iron is known to form the complex anion $[Fe(C_2O_4)_3]^{3-}$. The ability to form such complexes appears to be an essential property for a satisfactory mordanting assistant, and the usual theory that addition of acid to a mordanting bath simply suppresses hydrolysis of the salts by lowering the pH is clearly untenable.

The reason for the decline in the use of iron mordants with logwood is not clear, since they are superior to chrome mordants in fastness to light, and do not appear to be inferior in fastness to

milling. Compared with chrome mordants they have the disadvantage of requiring expensive assistants, and they probably require more care to obtain good fastness to rubbing. The shade on iron is somewhat deader than on chrome.

Rate of Exhaustion of Hæmatein and the Influence of pH

Dyeings of 3% hæmatein were made on patterns of flannel mordanted with (*a*) 3% potassium dichromate, (*b*) 1·5% potassium dichromate and 1·5% formic acid (85%), and (*c*) 5% ferrous sulphate, 1·5% copper sulphate, and 10% cream of tartar, for periods of 2, 5, 10, 20, 40, and 60 min., at 80°c. and 100°c., and the percentage exhaustion was then determined by analysis of the residual baths. The results are illustrated by Fig. 2.

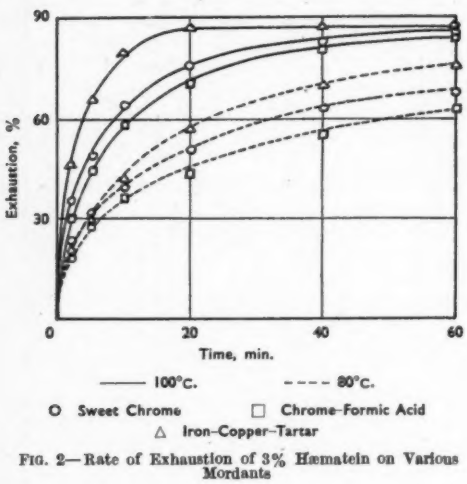


FIG. 2—Rate of Exhaustion of 3% Hæmatein on Various Mordants

The results show the rates of exhaustion of hæmatein on sweet chrome and chrome–formic acid mordants at 100°c. to be similar to those of ordinary level-dyeing acid dyes, but exhaustion on iron–copper mordant is much more rapid. Rates of exhaustion are appreciably lower at 80°c., the temperature effect being most marked with iron–copper mordant. Dyeing appears to be somewhat slower on chrome–formic acid than on sweet chrome mordant. It is considered that dyeing on any of the mordants should be started at a temperature not exceeding 80°c., and that exhaustion may then be adequately controlled by the rate at which the temperature is raised to 100°c.

The effect of the pH of the dyebath on the exhaustion of 3% dyeings of hæmatein was determined, using patterns of flannel mordanted with (*a*) 3% potassium dichromate and 6% tartaric acid, and (*b*) 5% ferrous sulphate, 1·5% copper sulphate, and 10% cream of tartar. The mordanted patterns were neutralised by treatment with 0·2% sodium bicarbonate solution, and dyed in 40-vol. baths with various additions of acid or alkali. The final pH values of the baths were measured, and the residual hæmatein was determined colorimetrically. The results are given in Table IX.

TABLE IX

Percentage Exhaustion of 3% Hæmatein at Different pH Values

Addition to Dyebath				pH at 20°c.	Exhaustion (%)
CHROME MORDANT					
1·0%	Sodium carbonate	...	...	7·13	96
0·15%	Acetic acid (30%)	...	...	5·76	97
1·2%	Acetic acid (30%)	...	...	5·30	96
1·0%	Formic acid (85%)	...	...	4·26	94
1·25%	Sulphuric acid	...	...	3·70	88
IRON–COPPER MORDANT					
4·0%	Sodium carbonate	...	...	9·42	93
2·0%	Sodium carbonate	...	...	9·05	94
None	...	...	...	6·03	99
1·0%	Acetic acid (30%)	...	...	5·53	98
1·0%	Formic acid (85%)	...	...	4·29	97
1·25%	Sulphuric acid	...	...	3·90	94

Baths containing sodium carbonate exhibited a brown colour which partly masked the purple colour of the hæmatein–tin complex, and the figures for percentage exhaustion are probably not reliable. Alkaline dyebaths also gave thinner shades than acid baths, although the exhaustion was apparently similar; this is probably due to destruction of hæmatein by oxidation in boiling alkaline solution. Below pH 7·0 exhaustion was not markedly affected by change in pH, but the fullest shades (and maximum fastness to rubbing) were obtained in faintly acid baths, and it is concluded that dyeing is best carried out at pH 6·0 approx.

Mixtures of Fustic and Hematine

In view of the general use of fustic for shading logwood blacks, it was thought that the effect of fustic on the fastness properties of Hematine should be determined. Dyeings were made with 2% Fustic Crystals No. 1 (YDC), alone and together with 6%, 8%, and 10% Hematine Crystals ZA, on mordants of (*a*) 3% potassium dichromate, (*b*) 1·5% potassium dichromate and 1·5% formic acid (85%), (*c*) 10% ferrous sulphate, 1·5% copper sulphate, 1·5% aluminium sulphate, and 10% cream of tartar; and (*d*) 5% ferrous sulphate, 1·5% copper sulphate, and 10% cream of tartar.

Fustic on chrome mordant gave a yellow shade of poor fastness to light (3–4), but of excellent fastness to milling (5) and very good fastness to potting (4–5). On iron–copper mordant, fustic gave a khaki shade which quickly became redder on exposure to light, with no further change on continued exposure; the shade was also reddened by alkali-treatment as in milling. Addition of fustic to Hematine was without effect on fastness to light on any of the mordants, and practically without effect on fastness to milling. Fastness to potting was slightly reduced, particularly with iron–copper mordants. It is concluded that fustic is very suitable for shading Hematine on both chrome and iron–copper mordants.

Other Metals as Mordants

This work was mainly of theoretical and historical interest, and consisted of a determination of the shades and fastness properties of dyeings of Hematine on mordants of various metals. These properties are summarised in Table X, the shades being those of 2% dyeings and the fastness properties those of 10% dyeings of Hematine ZA. Chromium, iron, and copper are included for the sake of completeness.

TABLE X
Properties of Hematine Dyeings on Various Mordants

Mordant	Shade	Light	Milling— Effect on Shade	Milling— Staining of Wool	Potting— Effect on Shade	Potting— Staining of Wool	Acid Cross-dyeing— Effect on Shade	Acid Cross-dyeing— Staining of Wool
Chromium ...	Dark blue ...	6	5	5	5	4–5	5	3–4
Iron ...	Dark blue ...	6–7	5	5	4–5	4–5	2–3	2
Copper ...	Bright blue ...	5	4–5	5	1	2–3	1	1–2
Tin	Purple ...	4	3	4–5	2	3–4	2	3
Aluminium...	Dull violet ...	4	2–3	5	1–2	2	1	2
Tungsten ...	Purple ...	4	2	4	1–2	3	1–2	2
Zirconium ...	Reddish blue	4	3	5	2	3–4	1–2	2
Nickel ...	Brownish grey	4	2–3	4–5	1	2–3	1	2
Molybdenum	Dark blue ...	6–7	1	3	2–3	1	5	1–2
Titanium ...	Black... ...	4–5	5		4–5	3–4	5	3–4

These fastness properties are liable to some variation with different mordanting methods. The difficulty in assessing the fastness to light of dyeings on chrome mordants, owing to the increasing rate of fading, has been referred to previously, and the same difficulty was found with molybdenum, and to a smaller extent with titanium mordants. The figures for fastness to light given in Table X were obtained by assessing when the patterns showed a distinct fade.

It had been observed that the fading of logwood blacks on iron mordants was accompanied by destruction of surface fibres, causing the cloth to appear threadbare. This effect was produced by all the iron mordants which were examined, irrespective of the method of application, but it was not marked until appreciable fading had occurred and is not considered to be of practical importance. A similar effect was also produced by tin, and to a smaller extent by aluminium, tungsten, and zirconium.

Chromium and iron are thus seen to be the only metals which give dyeings with logwood which are of sufficiently good general fastness to be of practical value. It is found with the majority of mordant dyes that the chromium lakes are of higher fastness than those of other metals, and logwood is probably exceptional in that its iron lake is not inferior to its chromium lake in fastness to light and milling.

APPENDIX

Fastness Tests

LIGHT— Patterns were exposed to daylight, under glass, facing south at an angle of 45° to the vertical. Four exposures were made, corresponding to distinct fades on S.D.C. light-fastness standards (*B.S.* 1006, Part 2) No. 4, 5, 6, and 7.

MILLING— The dyed wool was plaited with an equal weight of undyed wool and treated for 2·5 hr. at 50°C. in 40 vol. of a solution containing 50 g. soap flakes and 5 g. sodium carbonate per litre of distilled water. At 15-min. intervals the plait was squeezed lightly and milled by pounding in a mortar for 30 sec., this being done ten times. The plait was then rinsed and dried. The following dyeings were used as standards—

(1) 2% Orange III (IG)
(3) 6% Sulphoncyanine Black BB (IG)
(5) 5% Diamond Black PV (IG).

POTTING— A pattern of the dyed material (2·5 in. × 4 in.) and a similar piece of undyed wool were rolled tightly round a glass rod with the undyed material outside, and tied tightly at both ends. The roll was boiled for 1 hr. in 70 vol. of distilled water, rinsed, untied, and dried. The following dyeings were used as standards—

(1) 3% Disulphine Blue AS (ICI)
(3) 5% Diamond Black F (IG)
(5) 8% Diamond Black PV (IG).

ACID CROSS-DYEING— The dyed wool was plaited with an equal weight of undyed wool and boiled for 1 hr. in 50 vol. of a solution containing 2 g. Glauber's salt and 0·8 g. concentrated sulphuric acid per litre, rinsed, and dried. The following dyeings were used as standards—

(1) 2% Disulphine Blue VS (ICI)
(3) 2% Supranol Scarlet G (IG)
(5) 4% Indigosol O4B (DH).

PERSPIRATION— The test recommended by the Society's Fastness Tests Committee[19] was used.

ALKALI (STREET DIRT)— The dyeing was spotted with a mixture of 10 g. quicklime and 10 ml. ammonia (24%) per litre of distilled water, dried at room temperature, and brushed well. The patterns were compared for change of shade with the following standards—

(1) 2% Acid Green conc. S (IG)
(3) 2% Patent Blue V (IG)
(5) 3% Acid Alizarine Blue Black R (IG).

ACID SPOTTING— The patterns were spotted with (*a*) 10% hydrochloric acid, and (*b*) 40% acetic acid, and compared with patterns spotted with water, after 10 min. and after drying at room temperature. The following dyeings were used as standards—

(1) 3% Kiton Fast Green V (CAC)
(3) 2% Disulphine Blue VS (ICI)
(5) 5% Solochrome Black FS (ICI).

RUBBING— A pattern (5·25 in. × 5·25 in.) was rubbed for 2 min. (100 rev.) on the W.I.R.A. Abrasion Testing Machine with a disc of white calico at a pressure of 0·5 lb. per sq. in. The calico was then examined for staining.

Change of shade and staining of undyed material in wet-fastness tests were assessed according to the following scale—

Grade	Shade	Undyed Material
1	Strongly changed	Heavily stained
3	Slightly changed	Slightly stained
5	Unchanged	Unstained

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Discussion

WEST RIDING SECTION

Mr. R. HEATON: The addition of magnesium sulphate to logwood dyebaths might be expected to increase the depth of shade, since this apparently occurs in the case of metachrome dyebaths.

Mr. NEWSOME: The use of magnesium sulphate in metachrome dyeing depends on the formation of a magnesium–dye complex, which exhausts more rapidly than the dye itself, thus enabling exhaustion to be more or less complete before combination of the dye with chromium takes place. This occurs only above pH 7, and as the Hematine dyebath is neutral or faintly acid and the chromium is already on the fibre, there is no exact parallel between the two methods.

Mr. FRED SMITH: Does the fastness to milling of logwood black on chrome mordant vary with the pH of the dyebath?

Mr. NEWSOME: No milling tests have been made on logwood blacks dyed at different pH values, but dyeings made at low pH values were found to be less fast to rubbing than those made in neutral or faintly acid baths, indicating the deposition of dye lake on the surface of the fibres at low pH values, which might very well result in decreased fastness to milling.

Mr. H. KENNEDY: The lecturer has stated that aftertreatment with 1% copper sulphate increases the fastness to light. Does this aftertreatment affect the fastness to milling?

Mr. NEWSOME: Addition of copper sulphate to the mordant bath has little if any effect on fastness to milling, and aftertreatment with copper sulphate would not be expected to reduce the fastness.

Mr. E. BOOTHROYD: Is there a method for stripping logwood black from fur?

Mr. S. G. A. WISE: Logwood blacks on fur may be stripped by using a mixture of hydrochloric and oxalic acids.

Mr. S. PEEL: A properly dyed logwood black should be perfectly clean. Dirty blacks are usually caused either by insufficient washing after mordanting, or by the use of hard water. The use of calcium acetate, as mentioned in the lecture, is therefore undesirable. The increase in fastness to light of one point obtained by mixing Black T with Hematine scarcely justifies the increased cost, which is accompanied by decreased fastness to milling.

Mr. NEWSOME: The light-fastness scale is a geometrical one. A fastness of 7 is approximately twice as good as one of 6, so a one-point increase implies a very substantial improvement in fastness to light.

Mr. S. G. A. WISE: The lack of fastness to rubbing observed when hard water is used may be due to precipitation of tannins as calcium and magnesium salts.

SCOTTISH SECTION

A MEMBER: Are logwood blacks liable to rub? If so, what is the cause?

Mr. NEWSOME: Logwood on chrome mordant is perfectly clean if properly dyed, but dirty wool, insufficient washing after mordanting, or the use of hard water may result in poor fastness to rubbing. Logwood on iron appears to be intrinsically less fast to rubbing than logwood on chrome.

Dr. W. M. CUMMING: Can any information be given as to the reactions which occur in the "Sequence" (YDC) method of mordanting, which might explain the increased fastness to light? Further, has any weighting effect been observed when dyeing with logwood?

Mr. NEWSOME: We have no information with regard to the mechanism of mordanting by the "Sequence" method. Increases of weight of 4·2–5·0% have been obtained by dyeing with logwood, the higher figure being obtained with the "Sequence" method.

Mr. D. J. DUFF: The lecturer has stated that logwood is unusual among mordant dyes in that its iron lake is superior to its chromium lake in fastness to light. The other mordant dyes referred to, however, are azo compounds, and a more valid basis for comparison with logwood, which is a hydroxylated derivative of diphenylmethane, would probably be provided by synthetic hydroxylated di- or triphenylmethane dyes, a few of which are available commercially.

Mr. K. CAMPBELL: Speaking as one whose connection with logwood extends over fifty years, I regret that more work was not done earlier on the application side. The "Sequence" method has been found to be the best so far, and it is going to be followed up with a view to obtaining one-bath methods giving ease of application and dyeings of improved fastness. Recent work has shown that increased fastness is not to be obtained by modification of the structure of the hæmatein molecule. Some work will shortly be published on the production of more readily soluble logwood products. Much of the trouble referred to by other speakers may well have been due to the dye not being in true solution.

COMMUNICATION

The Dyeing Properties of Chlorinated Wool

I—Qualitative Experiments using Wool chlorinated at Various pH Values*

C. B. STEVENS, C. S. WHEWELL, and R. K. BRADLEY

A preliminary qualitative investigation has been carried out into the dyeing properties of wool treated in solutions of sodium hypochlorite at various pH values. It has been confirmed that, when using selected equalising acid, neutral-dyeing acid, direct cotton, and chrome dyes, wool treated in acid solutions of hypochlorite absorbs more dye than untreated wool when samples of both are dyed together in the same solution, whereas when treated under neutral or alkaline conditions it absorbs less dye and a resist effect is obtained. Treatment in hypochlorite solutions at certain intermediate pH values yields material with dyeing properties similar to untreated wool. Using basic dyes, the chlorinated wool absorbs more dye than the unchlorinated material irrespective of the pH at which the treatment is carried out.

During the last twenty years, and especially since the commercial development of the Woolindras process of dry chlorination, considerable attention has been paid to the dyeing characteristics of chlorinated wool. Earlier workers[1] on chlorination had shown that chlorinated wool generally dyes more deeply than unchlorinated material when the two are dyed together in the same bath, but later investigators, notably Lemin and Vickerstaff[2], Townend[3], Barritt and Elsworth[4], and Abbot, Crook, and Townend[5] have shown that the effects are complicated. Thus different results are obtained depending on the chemical treatment to which the wool has been subjected, the ease with which the dye can penetrate the fibrous structure, the constitution of the dye, and the conditions under which the dyeing is carried out.

With the exception of a recent study[6] of wool fabrics chlorinated by commercial methods, most of the work has been carried out on wool chlorinated in acid aqueous media or by chlorine gas, but it has been shown[7,8] that the reaction between wool and chlorine is greatly affected by the pH of the medium. It would be expected, therefore, that the dyeing properties of material chlorinated at various pH values would be of considerable interest. Abbot, Crook, and Townend state that wool chlorinated under alkaline conditions dyes less deeply than normal wool when the two types of material are dyed together, but there are few details of dyeing experiments carried out on material chlorinated under accurately described conditions. The first part of the present investigation consisted in examining the dyeing characteristics of wool treated in solutions of sodium hypochlorite at different pH values, and it was confirmed that, in general, when wool chlorinated under alkaline conditions and unchlorinated wool are dyed together in the same bath, the chlorinated material is dyed less deeply. Since acid-chlorinated wool is dyed more deeply than untreated wool when dyed together in the same solution, it would be expected that wool chlorinated at some intermediate pH would be dyed to the same depth of colour as unchlorinated when samples of each are dyed together. The second part of the work was carried out to find this critical pH value.

Experimental

PREPARATION OF FABRIC

A lightweight flannel of the following construction was used in all the experiments—

Warp	...	22 Yorkshire skeins woollen: 10·6 turns per in.; 29 ends per in.
Weft	...	20 Yorkshire skeins woollen: 10·6 turns per in.; 30 picks per in.
Weave	...	Plain.

The cloth, which had been finished commercially, was rinsed first in a solution of Calgon (5 g./litre) for 10 min. and then in water, after which it was scoured in a solution of Teepol (Shell) (3 g./litre) at 40°C. for 20 min., and finally washed, hydroextracted, and dried.

CHLORINATION

Although the treatment can be strictly described as chlorination only when carried out in acid media, for convenience the terms "chlorination" and "chlorinated" have been used to describe the treatments and treated material irrespective of the pH of the solutions employed.

All the chlorination treatments were carried out in the following way using a small dolly scouring machine. The cloth (100 g. approx.) was first brought to the appropriate pH by running it for 15 min. in a suitable aqueous solution to which a small amount of Calsolene Oil HS had been added to aid wetting. The requisite amount of sodium hypochlorite was then added during 15 min., and the treatment continued for a further 45 min. The material was in constant motion throughout the operation. The chlorinating solution was then drained off, and the cloth treated first in a 1·5% solution of sodium bisulphite for 15 min. to eliminate any residual chlorine or active chlorine compounds and then in cold running water for 12 hr. The fabric was then hydroextracted and dried. The pH of the chlorinating liquor was determined before the sodium hypochlorite was added and at the conclusion of the treatment, using a Cambridge Instrument Co. glass electrode.

Three series of chlorinations were carried out—

SERIES I—Samples of wool were chlorinated under acid and alkaline conditions using the following reagents—

* The substance of this paper formed part of lectures given by Dr. C. S. Whewell on 5th November 1948 to the Manchester Junior Branch (Mr. R. J. Hannay in the chair) and on 10th November 1949 to the West Riding Section (Mr. J. M. Goodall in the chair).

Acid Chlorination

Wool	96 g.
Sodium hypochlorite (100 g. available chlorine per litre)	34·7 ml.
Sulphuric acid (conc.)	12·9 ml.
Calsolene Oil HS (ICI)	9·8 ml.
Water	1500 ml.
pH of chlorinating solution	1·4
Percentage of chlorine present initially (on weight of wool)	3·4

Alkaline Chlorination

Wool	98 g.
Sodium hypochlorite (100 g. available chlorine per litre)	54·4 ml.
Borax solution (2%)	934·8 ml.
Calsolene Oil HS	9·9 ml.
pH of chlorinating solution	8·7
Percentage of chlorine present initially (on weight of wool)	5·7

SERIES II— Samples were chlorinated as above, i.e. at pH 1·4 and 8·7, using solutions containing 1, 2, 3, 4, and 5% of available chlorine on the weight of the wool.

SERIES III— Wool fabric was chlorinated at various pH values, the procedure being exactly as described above except that the borax solution was replaced by one of the solutions listed in Table I, which also indicates the amounts of chlorine present in the solution at the end of the experiment (the initial value was 3%). The chlorine was estimated volumetrically by the standard iodide–thiosulphate method.

TABLE I

Solution	Final Chlorine (%)	pH of Solution—After adding Hypochlorite	Final
5% Formic acid	0·04	2·32	2·34
5% Acetic acid	0·04	3·36	3·48
5% Sodium hexametaphosphate	0·0	5·64	5·53
2% Sodium borate + 2% boric acid	0·04	8·0	7·99
5% Sodium bicarbonate	0·02	8·82	9·10
1% Sodium carbonate	0·1	11·1	10·25

DYEING

In Series I, patterns of acid- and alkaline-chlorinated wool fabric and of untreated material were dyed together in the same bath using equalising acid, acid milling, neutral-dyeing acid, direct cotton, chrome, and basic dyes, but in Series II and III, pairs of patterns, one chlorinated and one unchlorinated, were dyed together. Several dyes were selected from each class: one group from the work of Barritt and Elsworth[4] was expected to give high contrast between acid-chlorinated and unchlorinated wool when these were dyed together in the same bath, while a second group was expected to give minimum contrast under the same dyeing conditions. Before dyeing, all the samples were wetted out in a warm solution of Calsolene Oil HS (2 g./litre), rinsed in cold water, and squeezed. For dyeing, a liquor : wool ratio of 50 : 1 was used throughout.

EQUALISING ACID DYES— A solution containing the requisite quantities of dye, sulphuric acid, and Glauber's salt was prepared, the temperature was raised to 50°C., and the wetted-out samples were placed in the liquid. Dyeing was continued for 45 min., during which the temperature was raised to 100°C., and the bath was maintained at that temperature for a further 45 min. When the dyeing was completed, the samples were removed, washed in cold water, and dried.

ACID MILLING, NEUTRAL-DYEING ACID, AND DIRECT COTTON DYES—The dyes were applied using the same general technique as that employed with equalising acid dyes, except that acetic acid or ammonium sulphate was used as dyeing assistant instead of sulphuric acid.

CHROME DYES— All the chrome dyes were applied by the afterchrome method. The cloth samples were placed in a solution containing the requisite amounts of dye and assistants at 50°C., the temperature was raised to 100°C. in 30 min., and dyeing then continued at that temperature for a further 45 min. The solution was then cooled to 70°C. by adding cold water, and potassium dichromate added, after which the temperature was again raised to 100°C. and chroming continued for 30 min. The samples were finally washed in cold water and dried.

PREMETALLISED DYES— The wetted-out samples were placed in a solution containing the requisite amount of sulphuric acid at 60°C. and treated therein for 15 min. The dye solution was then added, the solution was raised to boiling point in 30 min., and dyeing continued at the boil for 1 hr.

BASIC DYES— The wetted-out samples were dyed for 15 min. at room temperature in a solution containing acetic acid and the dye, after which the solution was heated to 80°C. during 30 min. and dyeing continued for 1 hr. at that temperature.

ASSESSMENT OF CONTRAST

The contrast between the pairs of dyed samples was assessed by visual examination. To express the differences observed, the following scheme has been adopted. In all cases, the unchlorinated dyed sample in each group has been taken as the standard of reference and is termed *neutral*. Those dyed, chlorinated samples which were dyed more deeply than the unchlorinated wool are described as *positive* while those dyed less deeply are described as *negative*. Since differences in contrast obtained were considerable, each type of contrast was subdivided into three grades according to degree as follows—

Darker ← +3 +2 +1 Neutral −1 −2 −3 → Lighter

This scale is arbitrary, and differences in contrast greater than + 3 and − 3 are not further subdivided. The purpose of the scale is simply to give a rough indication of the magnitude of the contrast obtained.

Results and Discussion

SERIES I— The results obtained on dyeing patterns (5 g.) of acid-chlorinated, alkaline-chlorinated, and unchlorinated wool together in the same bath are given in Table II together with details of the dyes and assistants used.

In general, the acid-chlorinated patterns were dyed more deeply than the unchlorinated samples, while the alkaline-chlorinated wool was dyed less deeply. The outstanding exception to this rule occurs when basic dyes are used, for both the chlorinated samples are dyed more deeply than

TABLE II

(The unchlorinated pattern in every case is taken as N)

Dyeing Class and Assistants used	Dye	Contrast obtained—Acid-chlorinated	Contrast obtained—Alkaline-chlorinated
Equalising acid	1·5% Disulphine Blue EGS (ICI) ...	+ 1	− 3
3% Sulphuric acid + 20% Glauber's salt	2% Naphthalene Scarlet 4RS (ICI)	+ 2	− 3
	2% Lissamine Fast Violet 2BS (ICI)	N	− 1
	1·5% Solway Ultra Blue BS (ICI)...	+ 1	− 1
Milling acid and Neutral-dyeing acid	1% Coomassie Milling Scarlet 5BS (ICI)	+ 3	− 3
3% Acetic acid + 20% Glauber's salt + 5% Ammonium acetate	1·5% Carbolan Blue BS (ICI)	+ 1	− 3
	1·5% Carbolan Yellow 3G (ICI) ...	+ 1	− 1
Direct cotton	1% Durazol Fast Yellow GRS (ICI)	+ 2	− 3
	1% Chlorazol Fast Eosine BS (ICI)	+ 3	− 3
10% Glauber's salt	1·5% Chlorazol Orange POS (ICI) ...	+ 1	− 2
	1·5% Icyl Orange GS (ICI)	+ 1	N
Chrome	3% Eriochrome Cyanine R (Gy)	+ 2	− 3
3% Acetic acid + 10% Glauber's salt + 1·5% Potassium dichromate	1% Solochrome Brilliant Blue BS (ICI) ...	+ 3	− 2
	2% Solochrome Orange GRS (ICI)	N	− 3
	2% Solochrome Red DS (ICI) ...	+ 1	N
Premetallised	2% Neolan Yellow 6GE (CAC) ...	+ 2	− 2
	1% Neolan Blue GG (CAC) ...	+ 2	− 1
8% Sulphuric acid	1·5% Neolan Violet 3R (CAC) ...	+ 3	− 2
	1·5% Neolan Yellow GR (CAC) ...	+ 2	− 2
Basic	0·5% Methyl Violet 2BS (ICI) ...	+ 3	+ 3
1% Acetic acid	0·5% Methylene Blue 2BS (ICI) ...	+ 3	+ 3

the unchlorinated material. The degree of contrast obtained varies with the particular dye chosen. Thus considerable contrast is obtained with Disulphine Blue EGS, Naphthalene Scarlet 4RS, Coomassie Milling Scarlet 5BS, Durazol Fast Yellow GRS, Chlorazol Fast Eosine BS, Eriochrome Cyanine R, Solochrome Brilliant Blue BS, and Neolan Violet 3R. Using Solway Ultra Blue BS, Lissamine Fast Violet 2BS, Carbolan Blue BS, Carbolan Yellow 3G, Chlorazol Orange POS, Icyl Orange GS, Solochrome Orange GRS, Solochrome Red DS, Neolan Yellow 6GE, and Neolan Yellow GR, considerably less contrast was obtained, particularly between the acid-chlorinated samples and unchlorinated material, although the same general decrease in contrast was noted between the alkaline-chlorinated wool and unchlorinated wool.

SERIES II— The results obtained indicated that the type of contrast obtained was independent of the percentage of chlorine present initially in the chlorinating solution, although some slight increase in contrast was observed with increasing amounts of chlorine.

SERIES III— The results obtained and other relevant data are given in Table III.

Examination of the dyed samples indicates that the pH at which the reversal of contrast takes place is dependent not only on the type of dye used

TABLE III

Class of Dye	Dye	Contrast at pH—2·3	3·5	5·5	8	9·2	10·2
Equalising acid	1·5% Disulphine Blue EGS	+ 1	+ 1	− 1	− 2	− 3	− 3
	2% Lissamine Fast Violet 2BS ...	N	N	N	N	N	N
Milling and Neutral-dyeing acid	1% Coomassie Milling Scarlet 5BS ...	+ 3	+ 3	N	− 3	− 3	− 3
	1·5% Carbolan Blue BS	+ 1	+ 1	− 1	− 2	− 3	− 3
Direct cotton	1% Durazol Fast Yellow GRS...	+ 3	+ 3	− 2	− 3	− 3	− 3
	1·5% Chlorazol Orange POS ...	+ 1	+ 1	− 1	− 2	− 3	− 3
Chrome	3% Eriochrome Cyanine R ...	+ 1	+ 1	− 1	− 3	− 3	− 3
	2% Solochrome Orange GRS...	N	N	− 1	− 2	− 2	− 2
Premetallised	2% Neolan Yellow 6GE	+ 2	+ 2	+ 1	N	− 1	− 2
	2% Neolan Violet 3R	+ 3	+ 3	+ 2	N	− 1	− 2
Basic	0·5% Methyl Violet 2BS	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3
	0·5% Methylene Blue 2BS	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3

but also on the particular dye. In the cases of Disulphine Blue EGS, Coomassie Milling Scarlet 5BS, Carbolan Blue BS, Durazol Fast Yellow GRS, Chlorazol Orange POS, Eriochrome Cyanine R, and Solochrome Orange GRS, the critical pH is about 4. Using material chlorinated at pH values below 4, with all dyes except Solochrome Orange GRS and Lissamine Fast Violet 2BS, the chlorinated pattern is dyed more deeply than the unchlorinated, but with these dyes the two patterns are approximately equal in depth. Contrast is generally not particularly marked with the above group of dyes if chlorination is carried out at pH values about 5·5, but when the pH of chlorination is in the region of 8 contrast again becomes evident, the chlorinated wool being dyed less deeply than the unchlorinated.

Lissamine Fast Violet 2BS, a dye known to yield solid shades on mixtures of unchlorinated and acid-chlorinated wool under suitable conditions, produces comparatively little difference in contrast on unchlorinated and chlorinated materials irrespective of the pH at which the chlorination is carried out. When Neolan dyes are used, the critical pH appears to be about 8, materials chlorinated at pH values greater than this showing "negative" contrast and those chlorinated at pH values 5·5, 3·5, and 2·3 showing "positive" contrast. With basic dyes, "positive" contrast is obtained whatever the pH at which the chlorination is carried out.

These differences in the dyeing behaviour of acid- and alkaline-chlorinated wool no doubt arise in part from the different mechanism involved in acid and alkaline chlorination. This aspect will be considered in Part II of this series of papers, but it is possible that the reduced absorption of dyes by alkaline-chlorinated wool is connected with an increase in the number of acidic groups in the wool produced by oxidation of disulphide bonds. When alkaline solutions of sodium hypochlorite are used for the treatment, the chlorinated wool has considerably greater base-combining capacity than either wool chlorinated in acid media or unchlorinated wool. Since, when using basic dyes, both acid- and alkaline-chlorinated wool is dyed more

deeply than unchlorinated wool when treated and untreated samples are dyed together, it appears that with acid and chrome dyes the operative factor is a difference in the rate of absorption of dye due to the increased accessibility of acid-chlorinated wool to dye particles resulting from modification of the physical structure of the fibres by the chlorinating treatment. The effect of increased accessibility would be most marked when applying under competitive conditions the relatively small amounts of dye used commercially.

The explanation of the reduced absorption of acid and chrome dyes by alkaline-chlorinated wool in the presence of unchlorinated material in terms of increased numbers of acidic groups in the treated wool resulting from oxidation of disulphide bonds is, however, incomplete, since it has been shown that silk treated in alkaline solutions of sodium hypochlorite is dyed less deeply than untreated silk when both are dyed together under the same conditions. Thus when samples of alkaline-chlorinated and untreated silk are dyed with Naphthalene Scarlet 4RS in the presence of sulphuric acid and Glauber's salt the chlorinated pattern is dyed less deeply than the unchlorinated.

DEPARTMENT OF TEXTILE INDUSTRIES
and
DEPARTMENT OF COLOUR CHEMISTRY AND DYEING
UNIVERSITY OF LEEDS

(*Received 9th December 1949*)

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[7] Whewell, Charlesworth, and Kitchen, *J. Textile Inst.*, **40**, P 769 (1949).
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CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Tendering of Nylon

The Editor,

SIR,

O. Newsome[1] presented a series of data showing the effect of various black dyes and various treatments with solutions of potassium dichromate on the photochemical degradation of nylon. Over the last three years, we have conducted a similar investigation, and in many instances our results agree closely with those reported in Newsome's paper, but in certain cases marked dissimilarities occur. It is considered that our results may prove of some interest, and they are reported below.

TABLE I

Fadeometer Exposure (120 hr.)

(Dyeings by "revised method"[2])

Dyeing	Reduction with $Na_2S_2O_3$	Lowering of Tensile Strength (%)
Undyed nylon (control)	—	52
0·5% $K_2Cr_2O_7$, 4% formic acid, 85°C. for 1 hr.	Reduced*	− 7
	Omitted	43
1·0% Solochrome Azurine BS ...	Reduced	15
	Omitted	40
1·0% Solochrome Brown RHS... ...	Reduced	− 3
	Omitted	2
1·0% Solway Blue Black BS	Reduced	3
	Omitted	15
1·0% Solochrome Red ERS	Reduced	3
	Omitted	23
1·0% Solochrome Yellow CS	Reduced	13
	Omitted	8

* 5% $Na_2S_2O_3$

Our tests were made on delustred British nylon, and the tensile strengths measured at 65% R.H. and 70°F. using a Goodbrand pendulum-type instrument. The method of afterchrome dyeing termed "the revised method" in Newsome's paper was used[2]. The dyeing process was not followed by any soaping treatment.

The results in Table I show the advantage which is gained by the introduction of a reducing treatment. Unfortunately, a dyeing of Solochrome Black WDFA was not included in this series. Other exposures, to daylight at Blackley, which qualitatively confirm the first series of results, included a dyeing of Solochrome Black WDFA. A selection of these results is given in Table II.

TABLE II

Daylight Exposure at Blackley (141 days)

(Dyeings by "revised method"[2])

Dyeing	Reduction with $Na_2S_2O_3$	Lowering of Tensile Strength (%)
Undyed nylon (control)	—	80·6
0·5% $K_2Cr_2O_7$, 4% formic acid, 85°C. for 1 hr.	Reduced*	29·4
	Omitted	53·4
1·0% Solochrome Red ERS	Reduced	24·1
	Omitted	36·9
10% Solochrome Black WDFA ...	Reduced	21·9
	Omitted	30·6

* 5% $Na_2S_2O_3$

From these results the following conclusions may be drawn—

(*a*) Compared with mordanted and reduced nylon, mordanted but unreduced nylon suffers increased degradation on exposure.

(*b*) Compared with undyed nylon, a chrome treatment exerts a protective effect. This effect is considerably greater if the chrome treatment is followed by an adequate reduction treatment.

Observation of the colour during exposure of nylon mordanted with potassium dichromate shows that the yellow coloration is rapidly destroyed and the nylon assumes an olive-green hue. This effect has been noted by Khandheria and Vaidya[3], who state that this colour change is accompanied by some degradation.

It is thought that the explanation of these observations is as follows— On exposure of the dichromate-mordanted nylon to light, the dichromate is reduced to the tervalent, chromic condition. Accompanying this change, there is a rapid degradation of the nylon. The nylon now contains tervalent chromium, which possesses the property of protecting the nylon from subsequent photodegradation. If the tervalent chromium is produced by reduction before exposure, by treatment with sodium thiosulphate, the initial degradation is eliminated.

Yours faithfully

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1st June 1950

[1] Newsome, J.S.D.C., **66**, 277 (May 1950).
[2] Hadfield and Sharing, *ibid.*, **64**, 381 (Dec. 1948).
[3] Khandheria and Vaidya, *J. Sci. Research*, India, **6**, (2), 24 (1947).

Notes

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 14th June 1950, the proceedings included the following items of interest—

Publications Committee— The resignation of Mr. J. T. Kidd was accepted with regret.

Other Committees— Acceptances of invitations to serve on various committees or to represent the Society on external bodies were reported (the names of the new members have been included in the lists published in the July 1950 issue (J.S.D.C., **66**, 345–347)).

Membership— Ten applications for ordinary and two for junior membership were approved.

Meetings of Council and Committees—July

Council— 12th
Finance— 12th
Publications— 18th
Diploma— 13th
Fastness Tests Co-ordinating— 13th
Leather Dyes— 10th
Perkin Centenary— 4th

Dr. A. J. Turner, C.B.E.

We are pleased to report the announcement in the King's Birthday Honours List of the award of the C.B.E. to Dr. A. J. Turner, director of research of the Linen Industry Research Association.

Imports of Dyes and Intermediates

The Dyer (**103**, 763 (16th June 1950)) reports that imports of synthetic dyes into the United Kingdom during January–March 1950 totalled 3647 cwt., their value being £330,608. The main countries of origin were Switzerland (2182 cwt., £242,455), France (916 cwt., £48,935), Germany (317 cwt., £28,296), and U.S.A. (105 cwt., £7241). The total imports of intermediates were 630 cwt. (£32,080), chiefly from Germany and U.S.A.

French-German-Swiss Fastness Meeting

According to the *Textil-Rundschau* for May 1950 (**5**, 219–220), the first joint meeting of the French, German, and Swiss fastness committees took place in Basle on 23rd February 1950. There had previously been four meetings between the Institut Textile de France and the fastness committee of the Schweizerischer Verband für die Materialprüfungen der Technik (S.V.M.T.), but this was the first time that a delegation from the Deutsche Echtheitskommission (D.E.K.) had been invited to join in the discussions, aimed at securing uniformity of methods of fastness testing.

The modifications to the Swiss standards, made as a result of these discussions with the French, are listed in the February 1950 issue of *Textil-Rundschau* (**5**, 63).

Twenty-third International Congress of Industrial Chemistry

Milan, 17th-23rd September 1950

This year the congress will be held in conjunction with the sixth *Congresso Nazionale di Chimica Pura ed Applicata*. The work will be organised in twenty-two sections, those likely to be of interest to readers of this *Journal* being—

2— Analytical chemistry
5— Physical chemistry
6— General chemistry
9— Organic chemistry
14— Chemistry of textile fibres and plastics
17— Chemistry of colouring matters
21— Chemical technology

Applications for admission and manuscripts of papers should be addressed to the Société de Chimie Industrielle, 28 rue Saint-Dominique, Paris VII, France. Participants can obtain a reduction of 20% on the French railways.

International Conference on Analysis and Testing

Paris, 20-24th November 1950

The pre-war *Journées internationales de l'Analyse et des Essais* will be revived this year at the Maison

de la Chimie in Paris, and will be accompanied by an exhibition of laboratory apparatus and industrial control gear. Manuscripts of papers should be submitted not later than 15th October 1950 to the Société de Chimie Industrielle, 28 rue Saint-Dominique, Paris VII, from whom further particulars and application forms may be obtained.

Chemical Works Safety Conference Scarborough, 29th September-1st October 1950

The above conference is being arranged for the Association of British Chemical Manufacturers by the Royal Society for the Prevention of Accidents, 131 Sloane Street, London S.W.1, from whom further particulars may be obtained.

Spectroscopy and Molecular Structure Cambridge, 25-28th September 1950

A general discussion on *Spectroscopy and Molecular Structure* and *Optical Methods of investigating Cell Structure* will be held in the Zoology Department of Cambridge University from midday on Monday, 25th September 1950, to midday on Thursday, 28th September 1950. Forms of application and advance proofs will be available on application to the Secretary, the Faraday Society, 6 Gray's Inn Square, London W.C.1.

New Books and Publications

The Standard Handbook of Textiles

By A. J. Hall. 3rd edition 1950. Pp. 296 with 228 Fig. London: The National Trade Press Ltd. Price, cloth, 21s. 0d.

The first edition of this book was published in 1946 and reviewed in this *Journal* the same year (**62**, 387). A second edition was published and reviewed in 1948 (**64**, 191).

The appearance of a third edition in so short a time indicates the demand for books of this type, and it is good to find that many of the minor errors in the first and second editions have now been corrected. The third edition is almost identical in its text and figures with the earlier editions, and very little new material has been included. In general the figures have been improved, a particularly useful change being the replacement of Fig. 20, Reeling Silk from Cocoons, which now enables the reader to form some idea of this process. The new matter includes references of a few lines each to polythene, Terylene, and the rotproofing of canvas ropes and cordage.

This book contains much interesting information and will be useful to a reader requiring a general picture of textile fibres and their manipulation. The size of the book prohibits a full treatment of the subject.

J. BARRITT

A.S.T.M. Standards on Industrial Water

Prepared by A.S.T.M. Committee D–19 on Industrial Water. Pp. viii + 134. Philadelphia: American Society for Testing Materials. 1949. Price, $1.75.

This is a collection of standard methods for sampling and analysis of industrial waters as published by the American Society for Testing Materials over a period of years. About half of the methods are still classified as "tentative", but the remainder have been adopted with or without revision after a suitable trial period.

The fact that the articles do not form a connected whole does not detract from their usefulness, as the majority of the important constituents are included. The methods, having been prepared by a committee of American experts, are authoritative, and give a wealth of detail which makes them suitable for use by chemists not possessing a specialised knowledge of this subject. Some selection has been necessary, and it should be observed that, for the most part, the methods do not apply to concentrates such as boiler waters, although space is given to methods for sampling boiler water and steam. Those interested purely in steam-plant water problems will find more information than provided here in the two British publications— *B.S.* 1328, *Methods of Sampling Water used in Steam Generation*, and *B.S.* 1427, *Tests for Water used in Steam Generation*— which form a comprehensive guide to the methods required in routine boiler-water analysis.

For dissolved oxygen, the methods described include a "Referee" method suitable for small concentrations and two modifications for less accurate work. The sampling bottle specified, with cocks at either end of a cylindrical body, has been abandoned in this country in favour of a sampling flask (see *B.S.* 1328 and 1427), owing to the greater ease of manipulation with the latter. The gravimetric sulphate method specified is of undoubted accuracy, but a more rapid, if less accurate, method is desirable for boiler waters. Similarly a rapid if not highly accurate method of hardness determination is called for in addition to the accurate calcium and magnesium methods described. In other instances, such as the determination of chloride ion, the method described is of more general application. Where colorimetric methods are included, such as, for example, those for nitrate, iron, and aluminium, the committee have chosen what they considered were the methods of most general application. It is not easy to please all workers, but where a number of alternative methods are available a passing reference to these alternatives would have been of value. In many laboratories where such determinations are regularly made on industrial waters, special conditions, such as the presence of fairly consistent contaminants, may make such alternatives preferable. An unfortunate omission is a colorimetric method for small quantities of phosphates, which frequently have to be determined when present to the extent of a few p.p.m.

Of particular interest are methods for examination of water-formed deposits by X-ray diffraction, two "corrosivity" tests, and two techniques for investigating bacteria of significance in industrial waters. The first corrosion test (National District Heating Association method) is suitable for assessing the durability of various engineering materials exposed to controlled conditions, while the second (United States Bureau of Mines method) is the "embrittlement detector", in which boiler water is allowed to concentrate by seepage in contact with a test specimen of metal under stress. The presence of iron bacteria is determined microscopically after the material has been washed with acid and stained with dyes to show up the cells. Sulphate-reducing bacteria are detected and estimated by growth in an anærobic culture medium.

The collection will be of value to all water chemists who have not ready access to the complete publications of A.S.T.M. in which the methods have previously appeared. C. W. DRANE

The Paint Industry in Germany during the period 1939-1945

BIOS Survey 22

By N. R. Fisk and H. W. Brown. Pp. 153. H.M.S.O. 1950. Price, 3s. 0d.

This survey is divided into four sections, viz. (1) Paints, Varnishes, and Printing Inks (subdivisions of this section deal with pigments and driers), (2) Waterpaints, (3) Cellulose Lacquers, and (4) Linoleum and Coated Fabrics. There is also a 16 pp. list of trade names, the chemical composition of each product being given. In addition to a list of the various BIOS, etc. reports used in preparing the survey, there is a list of FD documents dealing with this field of industry. There is an adequate index. The work of digesting the 200 or so available reports has been very well done, and an excellent guide to their contents provided, though the survey is so well written that, unless details are required, recourse to the original reports will usually be unnecessary. C. O. CLARK

Reports on German Industry

I.G. Farbenindustrie A.-G., Leverkusen Work on Organic Chemistry during 1942-44

FDX 807* (PB 74,621; Microfilm 91 L).

Microfilm of 94 laboratory and works reports, written in German in 1942–44. They deal largely with the manufacture of nylon, polyurethanes, *iso*cyanates, aliphatic dinitriles, phenolic compounds, diphenyl oxide derivatives, etc. useful for the manufacture of fibres, mothproofing and waterproofing agents, textile auxiliary and finishing agents, etc. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen 12th Scientific AKo (Azo Commission) Meeting 1937

Microfilms of papers and discussions thereon, in German, the titles being given below —

ACID DYES

FD 245/50*

(1) *Low-temperature Dyes— III*
(2) *Neutral-dyeing Acid Dyes applicable at* 80°C.
(3) *Synthesis of Neutral-dyeing Fast Acid Dyes*
(4) *Dyes from Derivatives of* o-cyclo-*Hexylaniline*
(5) *Continuation of Work on Supramine and Anthralen Dyes*
(6) *Wool Dyes from New Tribases* [*Isomeric Anisidine Tribase*]
(7) *Tests with Milling Dyes*
(8) *Tests on Various Dyes*
(9) *Use of 5-Amino-*p-*toluquinaldine in Preparation of Azo Dyes*
(10) *Wool and Cotton Dyes containing Thiosulpho Groups as the only Solubilising Groups*
(11) *Constitution of the Sulphonic Acids of 1-Amino-7-naphthol*
(12) *Dyes from 1-*p-*Carboxyphenylamino-7-naphthol-3-sulphonic Acid.*

CHROME DYES

FD 247/50*

(1) *The 2 : 3 Chromium Complex of* oo′-*Dihydroxyazo Dyes*
(2) *Azomethins containing Chromium— II*
(3) *Azo Dyes from* p-*Substituted Alkylphenols— II*
(4) *Chrome Dyes containing an* o-*Aminobenzenesulphoanthranilide Group*
(5) *Chrome Dyes from Azosalicylic Acid*
(6) *Chrome Dyes from Aminomethylumbelliferone*
(7) *Chrome Dyes from Methyldiphenylpyrazolone*
(8) *Work on Grey and Blue Chrome Dyes.*

DIRECT COTTON DYES

FD 250/50*

(1) *Contribution to the Understanding of Light Fastness in Azo Dyes*
(2) *Properties that determine the Fastness to Water of Substantive Azo Dyes*
(3) *Dyes of the Type of Sirius Supra Red 5B*
(4) *Experiments in the Sirius Supra Red Series*
(5) *Improving the Dischargeability of Columbia Fast Black G extra* (*Viscose Black G*)
(6) *Orange–Brown Trisazo Dye for Cotton*
(7) *Dye similar to Chlorantine Light Grey 4BLL*
(8) *Readily Soluble Cotton Dyes*
(9) *Cotton Dyes from the Condensate of* p-*Aminobenzeneazosalicylic Acid with 4-Nitrochlorobenzene-2-sulphonic or -2-carboxylic Acid*
(10) *Cotton Dyes to compete with Chloramine Brilliant Orange RS*
(11) *Cotton Dyes to compete with Jaune d'Or Direct 3R*
(12) *Cotton Dyes similar to Sirius Red 4B*
(13) *Sirius Dyes with Excellent Fastness to Water*
(14) *Sirius Supra Dyes from Aminoazo Dyes condensed with Dinitrostilbenedisulphonic Acid*
(15) [*Observations on the Coupling of Sulpho-*p-*aminosalicylic Acid and* p-*Aminosalicylic Acid with Naphtholsulphonic Acid*]
(16) *Dyes of the Type of Sirius Supra Orange.*

DEVELOPING DYES FOR COTTON AND MIXED FIBRES— SOLIDOGENS

FD 251/50*

(1) *Diazotisable Dyes from Mono- and Dimethoxymetazole Acids*
(2) *Dihydroresorcinol as a Developer for Diazotised Direct Dyes*
(3) *Substantive Diazo Compounds*
(4) *Fast Dyeing of Wool–Viscose Rayon Mixtures with Neutral Water-soluble Substantive Naphthols followed by Coupling with Diazo Compounds— III*
(5) *Coupling Components for Naphtol AS Dyeings on Wool–Viscose Rayon Mixtures*
(6) *Fast Dyeings by means of Self-coupling with Substantive Naphtholamines*

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

(7) *Fast Dyeings by means of Self-coupling with Substantive Naphtholamines containing Azo Groups*
(8) *New Solidogens.*

METALLIFEROUS COTTON DYES

FD 252/50*
(1) *New Benzo Fast Copper Dyes*
(2) *o-Aminoarylhydroxyacetic Acids as Azo Dye Components*
(3) *Copper Compounds of Azo Dyes from o-Dialkylaminodiazo Compounds*
(4) *Substantive Dyes from 2:6-Hydroxynaphthoic Acid*
(5) *Cotton Dyes with Triazole Rings*
(6) *Some Cotton Dyes*
(7) *Dyes containing Quaternary Groups* (two papers)
(8) *Red Benzo Fast Copper Dye*
(9) *Ergansoga Dyes fast to Perspiration*
(10) *Azol Printing Orange R* (two papers).

LEATHER DYES

FD 253/50*
(1) *Leather Dyes of Good Penetration*
(2) *Igenal Dyes*
(3) *Black Dyes for Leather*
(4) *Metal Complexes of Monoazo Dyes from Alkaline-coupled Sulphoalkyl-γ Acids*
(5) *Erganil Dyes*
(6) *Leather Dyes containing Thiosulpho Groups.*

PIGMENTS

FD 255/50*
(1) *Some Pyrazolone Pigments*
(2) *Work in the Hansa Yellow Group*
(3) *Transparent Hansa Yellow*
(4) *Diazo Pigments*
(5) *Concentration of Dye Pastes.*

ACETATE RAYON DYES

FD 256/50*
(1) *Dihydroresorcinol as Coupling Component*
(2) *Studies in the Cellitazol Series*
(3) *Water-soluble Acetate Rayon Dyes* (two papers)
(4) *Aminobenzotrifluorides as Components for Acetate Rayon Dyes*
(5) *Acetate Rayon Dyes containing Thiosulpho Groups*
(6) *Acetate Rayon Dyes having good Penetrating Powers.*

NAPHTOL AS— OXAZOLE, THIAZOLE, AND IMINAZOLE DERIVATIVES OF NAPHTHOLSULPHONIC ACIDS

FD 257/50*
(1) *Neutral Rapidogens*
(2) *Recent Work in the Naphtol AS Field*
(3) *Oxazole, Thiazole, and Iminazole Derivatives of Naphtholsulphonic Acids.*

DISCUSSION

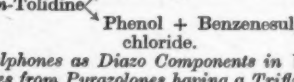
FD 258/50*
Discussions on the papers contained in the above summaries. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen 13th Scientific AKo (Azo Commission) Meeting 1938

Microfilms of papers and discussions thereon, in German, the titles being given below—

ACID DYES

FD 273/50*
(1) *Brown Nitro Dyes of the Azine Series*
(2) *Arylaminonaphtholsulphonic Acids as Azo Dye Components*
(3) *Neutral Fast Wool Dyes*
(4) *Supranol Yellow GG and other Neutral-dyeing Dyes*
Supranol Yellow GG has the constitution—



(5) *Aminosulphones as Diazo Components in Wool Dyes*
(6) *Acid Dyes from Pyrazolones having a Trifluoromethyl Group in the 4-Position*
(7) *Acid Dyes from Aniline-3-sulphomethylanilide-6-sulphonic Acid*
(8) *Miscellaneous Compounds*
(9) *Dyes from Derivatives of 2:3-Dichloro-1-nitrobenzene*
(10) *Supranol Browns*
(11) *Acid Dyes from Fast Brown V Base*
(12) *Dyes having Similar Properties to the Carbolans*
(13) *Azo Dyes containing [Long-chain] Aliphatic Radicals*
(14) *p-Aminophenylanthranil as a Diazo Component*
(15) [*Acid Anthracene Red G* versus *Brilliant Scarlet DH (NSK)*].

CHROME DYES

FD 274/50*
(1) *New Chrome and Metachrome Dyes*
(2) *Grey Chrome Dyes* (two papers)
(3) *Anomalous Chrome Dyes from Derivatives of β-Naphthylamine*
(4) *Chrome Dyes from 6-Aminomethylumbelliferone*
(5) *7-Aminocoumarans as Bases for Chrome and Palatine Fast Dyes*
(6) *Afterchrome Dyes [containing as Azo Components 2- and 3-Hydroxyfluorene, 2-Hydroxy-6-bromofluorene, 3-Hydroxy-6-methylfluorene, and 3:6-Dihydroxydiphenylene Sulphide]*
(7) *4-Nitro-2-aminophenol-6-sulphonic Acid→3-Hydroxydiphenylene Oxide—an Afterchrome and Metachrome Brown.*

DIRECT COTTON DYES

FD 275/50*
(1) *Symmetrical Azo Compounds from Aminonaphtholsulphonic Acids*
(2) *Cotton Dyes from Diaminoazobenzene*
(3) *Improving the I.G. Equivalents for Diphenyl Fast Bordeaux G, Diphenyl Fast Yellow GL and RL supra, and Direct Pink 3 BN*
(4) *Cotton Dyes from partly Acylated 2-Chloro-1:4-diaminobenzene-6-sulphonic Acid*
(5) *Azo Dyes from Bistrifluoromethylated Benzidines*
(6) *Cotton Dyes fast to Boiling*
(7) *Stilbene Dyes containing Triazole Rings.*

DEVELOPING DYES FOR COTTON

FD 288/50*
(1) *Avoiding Yellowing of Acetate Rayon when Dyeing its Mixtures with other Fibres with Dyes developed with β-Naphthol*
(2) *Red Diazo Dyes*
(3) *A New Group of Water-soluble Dyes*
(4) *Improving the Wet-fastness of Soluble Dyes by Simple Aftertreatment*
(5) *1-Phenyl-5-hydroxytriazole as a Component for Yellows.*

METALLIFEROUS DYES

FD 289/50*
(1) *Azo Dyes from Aminopyrazoles— Benzo Fast Copper and Milling Red Dyes*
(2) *Benzo Fast Copper Dyes from 2-Aminophenoxyacetic Acid and its Derivatives coupled with Components giving Affinity for Cellulose*
(3) *o-Aminoarylhydroxyacetic Acids as Components for Aftercoppered Polyazo Dyes*
(4) *Brown Benzo Fast Copper Dyes*
(5) *Grey Benzo Fast Copper Dyes*
(6) *Metal-complex-forming Azo Dyes having Substantive Pyrazolones as Coupling Components*
(7) *Bispyrazolones from Benzidines and 4:4'-Diaminostilbene-2:2'-disulphonic Acid and Dyes therefrom*
(8) *Benzo Fast Copper Dyes having Aminophenyl-3-phenyl-5-pyrazolones as Intermediates*
(9) *Some Benzo Fast Copper Dyes*
(10) *6-Chloro-2-aminophenol-4-carboxylic Acid as Diazo Component for Benzo Fast Copper Dyes*
(11) *Dyes from three Newly Prepared Pyrazolones*
(12) *Benzo Fast Copper Dyes from Nitrohydroxybenzoyl Chlorides*
(13) *Carboxyaminobenzoyl-J Acids*

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

(14) *o'-Carboxyaminobenzoylphenylenediaminecarboxylic Acids as Diazo Components for Benzo Fast Copper Dyes*
(15) *1-Amino-3-naphthol-7-sulphonic Acid as Intermediate for Azo Dyes*
(16) *Brown Condensation Dyes of the Stilbene Series*
(17) *Ergansoga Dyes*
(18) *Cheap Substitute for Ergansoga Merah Tocah 4 RL*— o-Amino-*p*-Sulphosalicylic acid→Cleve's acid→Salicylic acid.

DYES FOR MIXTURES OF WOOL AND COTTON AND/OR VISCOSE RAYON

FD 290/50*
(1) *Self-coupling Naphthol-amine-azo Dyes*
(2) *Self-coupling Substantive Naphtholamines*
(3) *Aminoazo Dyes by the Acid Self-coupling on the Fibre of Aminonaphthols*
(4) *Self-coupling Aminoazo Dyes of the J Acid Series having Coupling Groups outside the J Acid Nucleus*
(5) *Aminonaphtholsulphonic Acids as Components for Self-coupling Dyes*
(6) *Self-coupling Dyes for Wool–Viscose Staple Fibre Mixtures*
(7) *Iminazole Derivatives of 1:2-Diamino-5-naphthol-7-sulphonic Acid*
(8) *Unsuccessful Attempts to prepare Self-coupling Diazoamino Compounds*
(9) *Dyeing Wool–Viscose Staple Fibre Mixtures with Azoic Dyes*
(10) *An Azoic Navy Blue for Wool–Viscose Staple Fibre Mixtures*
(11) *A New Aftertreatment for Improving the Fastness of Diazotisable Azo Dyes*
(12) *Direct Dyes of Good Wet Fastness when aftertreated with Chrome*
(13) *6-Sulpho-2:3-hydroxynaphthoic Arylides as Coupling Components for Azoic Dyes on Wool–Viscose Rayon Staple Fibre Mixtures.*

LEATHER DYES

FD 291/50*
(1) *Black Mono and Diazo Dyes for Leather from the Sulphomethyl and Sulphoethyl Derivatives of 1-Amino-7-naphthol-3-sulphonic Acid*
(2) *Leather Dyes from Igenal Brown IGG Base*
(3) *Metalliferous Monoazo Dyes from o-Aminophenols* $\xrightarrow{\text{Alkali}}$ *Sulphoalkyl-γ Acid Derivatives* $\xrightarrow{\text{Alkali}}$ *γ Acid*
(4) *Erganil Dyes* [— *Attempts to produce a Green-toned Grey*]
(5) *Erganil Dyes from Dihydroxy-J Acids and from the Imide of J Acid*
(6) *Grey to Black Erganil Dyes*
(7) *Blue Leather Dye* [*using 1:8-Aminonaphthol-2:4-disulphonic Acid as an Intermediate*]
(8) [*Igenal Brown JR.B*]
This is the copper complex of —
2-Anisidine-4-sulphonic acid→Phenyl-γ acid
(9) *Leather Dyes of Good Penetration* [*from 2-Halogeno-4-nitroaniline-6-sulphonic Acid→Substituted Anilines*].

ACETATE RAYON DYES

FD 297/50*
(1) *4:5-Dinitro-2-aminophenyl Methyl Ether as Component for Acetate Rayon Dyes*
(2) *Dyes containing N-Alkylphenylamino-2:3-propylene Oxides as Coupling Components*
(3) *3-Arylaminotetrahydrofurans as Intermediates for Acetate Rayon Dyes*
(4) *3-Arylamino-1-hydroxybutanes and 3-Arylamino-1:2-dihydroxybutanes as Intermediates for Acetate Rayon Dyes*
(5) *Celliton Dyes having Aminophenyldiguanides as Intermediates— Basic Dyes having 4-Aminophenylmethyldiguanides as Intermediates*
(6) *Acetate Rayon Dyes from* m-*Aminophenylmethylcarbinol*
(7) *Water-soluble Acetate Rayon Dyes containing no Acid Groups*
(8) *Cellitazols from 5-Nitro-2-anisidine→Dihydroxyethyl-*m-*toluidine or other Tertiary Base subsequently reduced*
(9) *Cellitazols from 4:4'-Diaminoazobenzene*
(10) *Water-soluble* [*Yellow to Orange and Red to Bordeaux*] *Acetate Rayon Dyes*
(11) *Self-couplers on Acetate Rayon*
The compounds prepared and tested were (i) naphthols containing a heterocyclic ring, (ii) naphthols containing no heterocyclic ring, (iii) aroylacetanilides, (iv) phenylmethylpyrazolones, and (v) hydroxyquinolines
(12) *Water-soluble Acetate Rayon Dyes which form Complexes with Heavy-metal Salts.*

PIGMENTS— DYES FOR ACETATE AND VISCOSE RAYON

FD 300/50*
(1) *Helio Red BL* (o-*Toluidine→Azuric Acid, Calcium Lake*)
(2) [*Ammonium Persulphate as a Bactericide in*] *Pigment Pastes* [*particularly in Hansa Yellow GT paste*]
(3) *Influence of F Acid on the Coupling of* p-*Nitroaniline with β-Naphthol*
(4) [*Permanent Carmine FB* (*Fast Red Base ITR→Naphtol AS–ITR*) *and Similar Pigments from Naphtol AS–ITR*]
(5) [*General Survey of Dyes for Acetate and Viscose Rayon — Grading and Dispersal of Azo Pigments*]
(6) *Some Lake-forming Azo Dyes*
(7) *Chromiferous and Cupriferous Pigments*
(8) *Pigments* [*from Acyl Compounds of 1:3-Diaminobenzene-4-sulphonic Acid and Acylaminopyrazolones*]
(9) *Zapon Fast Yellow CGG*— Dicyclohexylamine salt of orthanilic acid→carboxypyrazole acid 2 (Fast Light Yellow 3G)
(10) [*Carboxyamides as Solvents for the*] *Metallisation of Unsulphonated Azo Dyes*— Zapon Fast Red BE is the chromium compound, prepared in formamide, of 5-nitro-2-aminophenol→1-phenyl-3-methyl-5-pyrazolone
(11) *Complex Metal Compounds of Unsulphonated Azo Dyes*
(12) *Dimethyl Palm-kernel Fatty Amine as Precipitant for Zapon Fast Dyes*— Zapon Fast Black NCB is the chromium complex of pic-amic acid→2:4-naphtholsulphonic acid, treated with dimethyl palm-kernel fatty amine salt
(13) *Sudan Dyes.*

MISCELLANEOUS AZO DYES

FD 301/50*
(1) *Nitration of Esters of Naphtholsulphonic Acids*
(2) *2:5:8- and 2:8:5-Aminonaphtholsulphonic Acids and Dyes from them*
(3) *New Process for Preparing 2-Naphthol-4-sulphonic Acid and its Derivatives*
(4) *Diazotisation of 6-Nitro-3-toluidine-4-sulphoethylanilide and 4-Nitro-2-sulphoethylanilide* [*in Glacial Acetic Acid with Hydrochloric and Sulphuric Acids respectively*]
(5) *Action of Phosgene and Phosgene–Pyridine* [*Mixtures*] *on Azo-β-naphthol Couplings*
(6) *Benzo Fast Orange and Benzo Fast Scarlets*
(7) *Improvements in* [*Manufacture of Vesuvin BL new, Diazo Dark Blue 3B, and Columbia Fast Black G extra*].

NAPHTOL AS DYES

FD 302/50*
(1) *Naphtol AS Dyes soluble in Organic Solvents— II*
(2) *Recent Work* [*by the I.G. and by competitors*] *in the Naphtol AS Field.*

DISCUSSION

FD 303/50*
Discussions on the papers summarised above.

C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

Vereinigte Glanzstoff Fabriken, Obernburg
Viscose Rayon—Perlon

FDX 797* (PB 74,216; Microfilm 302D).

The first part of this microfilm contains 28 reports, in German, written in 1937–38, mainly in connection with the production and processing of viscose rayon, with very full reports on the production of textile assistants from petroleum and on adding fish protein to viscose spinning solutions. The second part contains 34 reports written in 1941–44 on various aspects of the production of viscose rayon and polyamide fibres. C. O. C.

I.G. Farbenindustrie A.-G., Bitterfeld
Plasticisers for Plastics

FDX 814* (PB 73,491; Microfilm BB123).

Microfilm of 40 reports, written in German during 1937–43, mostly dealing with plasticisers for plastics. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Analytical Methods approved during 1939–41

FDX 790* (PB 70,062; Microfilm 22G).

A microfilm of a very large number of inorganic and organic analytical methods (892 pp., in German) approved for use during 1939–41. C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1 or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Grinding Paint, Cellulose, etc. J. McIntyre. *B.P.* 636,829.

Stretching Polyacrylonitrile Filaments, etc. I.C.I. Ltd. *B.P.* 637,593.

Fibre Scouring and Washing Bowl. E. H. Brooks Snr., E. H. Brooks Jr., and E. H. Thompson. *U.S.P.* 2,493,944.

A series of apertured rolls are mounted transversely to the tank containing the scouring liquor, in which they are partly immersed. Beneath each roll there is an arcuate baffle secured to the tank so as to form a series of scouring chambers. Above each roll there is a cover secured to the tank. A weighted pressure plate is suspended from each cover, to which it is pivoted, and ends adjacent to the scouring chamber. Between each pair of rolls there is a rotatable perforated roll mounted transversely to the tank. The wool passes between each of the apertured rolls and the corresponding baffle, and is moved from one chamber to the next by the perforated rolls. Extremely efficient scouring is obtained. C. O. C.

Continuous Wet Treatment of Loose Fibres. W. R. Adams and Johnson & Johnson. *U.S.P.* 2,493,740.

A self-sustaining plug of loose fibres is formed in a conduit, to which the treating liquor is supplied continuously behind the plug. Sufficient pressure of the liquid is maintained behind the plug to eject the plug progressively from the conduit, the liquid being supplied at sufficient volumetric rate to cause it to flow through the plug at substantial linear velocity while the plug is being ejected. The plug is rebuilt continuously by supplying loose fibres to the liquid at the same rate as those in the plug are being ejected. C. O. C.

Drying Textile Materials. Courtaulds Ltd. and Industrial Rayon Corpn. *B.P.* 636,864.

A thread-advancing reel comprises two reel members mounted on axes which are offset and skew to each other, each reel member having a series of bars which interleave and co-operate to form a cylindrical supporting surface, on which the thread is advanced in several spaced helical turns. The reel has a thermostatically controlled inner heating chamber with an inlet for heating medium and an outlet for exhaust gases.

B.P. 636,865.

A drying reel has two interdigitating sets of bar members offset and inclined to each other, over which the thread passes, one set having passages through which heating fluid is continuously circulated.

B.P. 636,866.

Both sets of bar members are tubular and may be formed in pairs from one member having a 180° bend, and heating fluid is continuously circulated through in close proximity to the thread. J. W. B.

Drying Yarns or Ribbons. R. F. Conaway, I. V. Hitt, and Du Pont. *U.S.P.* 2,495,053.

Individual ends of yarn, etc. are rapidly dried by being drawn at high speed and under low tension over curved dryer plates heated to $> 100°C$. The curvature of the plates is adjusted to obtain maximum efficiency, the drying rate and yarn tensions being so balanced as to give optimum drying conditions. C. O. C.

Winches. L. J. Lederer and L. J. Lederer Jr. *U.S.P.* 2,488,208.

The winch of a dyeing machine is covered by spirally winding a narrow strip of a plastic material around it. Such a covering has a longer life than the cotton covering hitherto used, and does not need bleaching when a change of colours is made. C. O. C.

Open-width Dyeing Machine. J. Dungler. *B.P.* 636,544.

The fabric passes in open width through the nip of at least one pair of horizontal pad rollers while being fed along a spiral course such that it passes at least twice in the same direction through the pad rollers. This enables fabric to be passed through the dyebath continuously and in the same direction for as many times as necessary. C. O. C.

Padding Machine. J. Dungler. *B.P.* 636,010.

The rollers are mounted in a support which can be swung about the axis of a stationary roller so that vertical or horizontal arrangement of the rollers can be obtained at will. C. O. C.

Preventing Bands, Blankets, Paper Webs, etc. from "Wandering" on Rollers. E. N. Mason & Sons Ltd. *B.P.* 635,401.

Multicolour Printing Machines. A. I. Sark. *B.P.* 634,213.

In printing machines whose printing surface is composed wholly or partly of the printing compositions so that a multicoloured print is obtained by one impression, the intensity of the print depends upon the time of contact and the pressure between the printing surface and the material to be printed. Both factors can be varied by providing a deformable and resilient printing bed, the extent of deformation of which is under control. Such a bed can consist of a deformable rubber roller filled with liquid. C. O. C.

Fabric Winding or Batching. British Celanese Ltd. *B.P.* 634,515.

A guide roll driven by the fabric passing over it guides the fabric to a take-up roll. Rotation of the guide roll operates a device which can cause the axis of the roll to oscillate angularly about a point between the ends of the roll. C. O. C.

Cloth-drying Machine. J. Dungler. *B.P.* 634,322.

A single-cylinder drying machine which can replace a multi-cylinder machine, with considerable reduction in steam consumption, consists of a casing containing a heated rotary drying drum and a set of nozzles placed concentrically outside the drum. The orifices of the nozzles are close to the surface of the drum, on to which they direct hot air. The cloth to be dried passes between the surface of the drum and the nozzles. C. O. C.

Infra-red Drying of Coated Fabrics or Paper. T. T. Baker and T. H. Dixon & Co. Ltd. *B.P.* 635,565.

Open-width Drying Machine. B. Offen. *B.P.* 636,767.

The machine does the drying in two stages. In the first flames are directed towards the material; in the second hot

air is directed over its surface. Relatively cold air is automatically circulated in the first stage whenever passage of the material through the machine is interrupted. If the material is stopped in the first stage, then the burners automatically move away from it. C. O. C.

Cloth-guiding Mechanism for Clip Stenters. J. Dean. *B.P.* 634,375.

A photoelectric cell, or a finger, is associated with a thruster, preferably of the electric hydro type, which adjusts the clips into correct registry with the selvedges should the latter get out of line. C. O. C.

Control of Drying Machines. Fielden (Electronics) Ltd. and L. Witcombe. *B.P.* 636,092.

A voltage dependent on the moisture content of the material is fed to an electronic instrument, which controls a relay, this starting a motor which drives the speed control of the machine in the appropriate direction. The arrangement is such that the period for which the motor runs is determined by the variation of the moisture content from a determined value. The motor is actuated at intervals, the lengths of which vary inversely with the speed of the machine. C. O. C.

Cooling the Fan Shaft Bearings of Drying Machines. Petrie & McNaught Ltd. and R. Petrie. *B.P.* 636,509.

Spray Damping Machine. A. M. Phillips. *B.P.* 634,619.

Atomiser heads are seated on the exterior of a pipe containing passages for air and water. Separate outlets from these passages terminate in the seating surface of the pipe so as to register with appropriate receiving passages in the atomiser heads. C. O. C.

Continuous Decatising. G. Haeberlin. *U.S.P.* 2,494,807.

The fabric is run across part of the periphery of a perforated cylinder, with which it is held in contact by a blanket. High-pressure steam is blown on to the blanket from a series of nozzles parallel to the axis of the cylinder, simultaneously with the exertion of suction from within the cylinder. An arcuate face plate concentric with the cylinder surrounds the steam nozzles. Very uniform treatment is obtained.

U.S.P. 2,494,808.

In a blanket and endless-carrier type of decatising machine the steam is supplied by nozzles across the blanket exit. The nozzles are so placed that they eject the steam counter to the direction of travel of the blanket and at an angle away from the blanket. This enables decatising to be speeded up and removes any fear of marks from condensation droplets. C. O. C.

Stencil Printing Machine for Textiles. J. I. Marek and L. Steinberg. *B.P.* 635,744.

An endless belt serves as the printing table. When the stencil frames are lifted at the end of a printing operation, the edges of that portion of the belt actually supporting the fabric being printed are gripped by devices which move the belt to bring the fabric to the next printing position. These devices relax their grip on the belt as the stencil frames are lowered on to the fabric. C. O. C.

Steaming Textiles. G. P. Vincent, A. L. Dubeau, and Mathieson Chemical Corpn. *U.S.P.* 2,494,731.

A closed steam chamber contains several lateral conveyors one above the other. The fabric is fed in open width into the chamber so that it falls in upright accordion folds on to the top conveyor. At the discharge end of every conveyor but the last there is a device for transferring the folded cloth to the receiving end of the conveyor beneath it. The fabric is led out of the chamber from the bottom conveyor. Very uniform steaming is achieved without danger of crease marks. C. O. C.

Steaming Fabrics. T. G. Brown. *B.P.* 637,211.

A connection is provided from the steaming vessel to an evaporator, from which the steam passes through a drier. A connection is taken from the top of the drier to a steam-energised thermo-compressor, which extracts vapour from the drier. The vapour passes with steam into the steamer, replacing a large proportion of the boiler steam and resulting in a large saving of fuel. C. O. C.

Web-coating Apparatus. Kodak Ltd. and L. P. Morey. *B.P.* 636,673.

An arrangement is described whereby the pan containing the coating solution can be rapidly replaced by another pan containing the same or a different coating solution without causing any appreciable agitation in the surface of the solution in the pan moving into the coating position. C. O. C.

Preboarding Nylon Hose. Etablissements M. Heliot. *B.P.* 635,722.

Groups of metal shapes arranged in circles are mounted at the apices of a triangular plate. The plate rotates about a tubular upright acting as a piston housing for the hydraulic vertical movement of a metal dome, such that each set of shapes may be successively enveloped for the steaming operation. A metal disc situated below the rotary plate and opposed to the dome is raised by a piston, and engaged by hooks when the latter is lowered, a fluid-tight seal being formed when the two are engaged. G. E. K.

Hardening Machine for Felt Hoods. A. J. Evers. *U.S.P.* 2,495,923.

Flatplate Ironing Machine. H. L. Newell and General Electric Co. *U.S.P.* 2,495,641.

Regulating the Concentration of Fibrous Suspensions. K. A. Karlsson. *B.P.* 636,957.

A quantity of the fibrous suspension, e.g. papermaking stock, is introduced continuously or intermittently into an annular vessel, rotating about a horizontal shaft carried by an arm of a balance and fitted with a concentric annular overflow. The quantity of suspension moves the vessel in proportion to its concentration, and the balance, which is loaded with a pendulum weight, is caused to deflect. A curved slot mounted on the shaft, which is turned by the deflection of the beam, engages a projection of a mechanically driven member reciprocating within a fixed range, and thus controls a dilution valve or means for adding solid to the suspension. The apparatus need not include any part immersed in the suspension to be controlled. S. V. S.

Continuous Production of Synthetic Twisted or Untwisted Fibres and Yarns suitable for Direct Use. B. Borzykowski and Swiss "Borvisk" Co. (VI, p. 455.)

II—WATER AND EFFLUENTS

PATENT

Flocculation of Solids in Aqueous Suspension. De Directie van de Staatsmijnen in Limburg. *B.P.* 634,440.

The clarifying effect of starch sol is increased if before adding it to the raw water it is treated with an acid of strength not $> 0{\cdot}01$ g.-equiv. per litre of 1% starch sol and care is taken not to use excess of starch sol. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Emulsion Reactions: the Hydrolysis of Wool Wax. J. L. Horner and E. V. Truter. *Nature*, **165**, 771 (13th May 1950).

In a water-in-oil emulsion, hydrolysis proceeds much more rapidly than in an oil-in-water emulsion; e.g. 1 g. of wax is hydrolysed completely in 6 hr., as against only ~ 40% reaction after 100 hr. The difference is not due solely to the greater concentration of alkali as reactant, but is determined mainly by changes in the nature of the interface and the effect of reaction products upon it. Experiments are now described in which these effects have been isolated. In practice, the hydrolysis of wool wax need not be carried out with highly concentrated aqueous NaOH solutions, 2N-NaOH in 4N-NaCl solution at 60°C. being just as effective as 4N-NaOH at the same temperature. H. H. H.

Problems in the Development of Efficient Woollen-fibre Lubricants. P. J. Martin. *Amer. Dyestuff Rep.*, **39**, P 223–P 228 (3rd April 1950).

The routine tests employed in the development of wool oils are described. In addition, certain specially designed tests are required to develop superior wool oils, e.g., for fulling and scouring performance, fibre friction testers, condenser-tape testers, and electrostatic voltmeters. Controlled mill-scale operations are used to assess differences in wool oil performances not normally discerned in commercial mills. Significant differences in performance were found in oils all of which were acceptable in mill operations. W. J. M.

Tick-repellents. M. M. Cole and C. N. Smith. *J. Econ. Entomol.*, **42**, 880–883 (1949): *Chem. Abs.*, **44**, 3650 (25th April 1950).

Of various tick-repellents tested against loose-star ticks, *Amblyomma americanum*, butyl 3:4-dihydro-2:2-dimethyl-4-keto-1:2*H*-pyran-6-carboxylate (Indalone), 2-phenoxyethyl *iso*butyrate, hexyl mandelate, and ethyl β-phenylhydracrylate were most effective and safe for use on skin or clothing. The first-named compound was the most consistently effective; it was better applied in acetone solution than as an emulsion. C. O. C.

PATENTS

Carding and Spinning Lubricants for Wool or Mixtures of Wool with other Fibres. Nopco Chemical Co. *B.P.* 634,588.

A composition for lubricating wool during carding and spinning, which serves also as the milling and scouring agent for the fabric made from the lubricated wool, consists of a non-resinifying oil mixed with the condensate of 1·5 mol. of diethanolamine, *N*-ethylmonoethanolamine, di*iso*propanolamine, or 2-amino-2-methylpropanol, and the equivalent weight of an aliphatic acylating substance containing > 7 C in its acyl group, e.g. coconut acid. C. O. C.

Dry Starch Preparations soluble in Cold Water. N.V. W. A. Scholten's Chemische Fabrieken, J. Lolkema, and W. A. van der Meer. *B.P.* 634,368.

Compositions which dissolve readily in cold water, to yield solutions which on adding an acid catalyst produce water-insoluble finishes when dried on textiles, are made by mixing cold-swelling starch with an aldehyde and/or a substance yielding an aldehyde and with a substance (other than an aminotriazine) capable of forming a synthetic resin with the aldehyde. C. O. C.

Size. G. D. Jefferson, R. D. Fine, and Atlas Powder Co. *U.S.P.* 2,495,845.

A size particularly useful for nylon knitting yarns comprises a water-sensitive hydroxylic polyvinyl resin, boric acid, a water-insoluble scourable wax which is incompatible with the resin, and a non-ionic water-soluble emulsifying agent. C. O. C.

Cellulose Ethers. Courtaulds Ltd. and J. H. Macgregor. *B.P.* 636,295.

Water-soluble mixed cellulose ethers containing the cyanoethyl group are prepared by dissolving a water-insol., alkali-sol. cellulose ether, containing not > 1 ether group per anhydroglucose unit, in a dil. aq. alkali hydroxide soln. containing not > 6% by wt. of caustic alkali, and treating the soln. with 0·1–2·5 mol. of acrylonitrile per anhydroglucose unit. They are useful as sizes and starch substitutes. J. W. B.

Oleonitrile Derivatives having Surface-active Properties. W. Kaplan and Sun Chemical Corpn. *U.S.P.* 2,495,105.

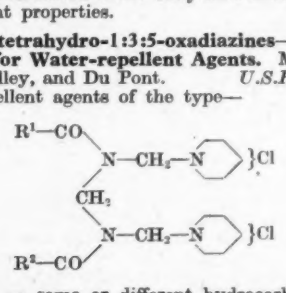
Sulphonated, sulphated, or, less desirably, phosphated or borated high-mol. wt. aliphatic nitriles, e.g. sulphonated oleonitrile, are excellent surface-active materials. C. O. C.

Wetting and Detergent Compositions. American Cyanamid Co. *B.P.* 636,462.

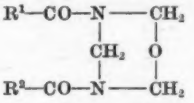
Mixtures of sulphosuccinates MOOC·CH(SO_3M)·CH_2·COOR (M = alkali metal or NH_4, R = aliphatic radical of 12–18 C) and water-soluble salts of Li, Mg, Be, Cr, and/or Co are readily soluble in water. They have excellent wetting and detergent properties. C. O. C.

***NN'*-Diacyltetrahydro-1:3:5-oxadiazines—Intermediates for Water-repellent Agents.** M. Hunt, H. W. Bradley, and Du Pont. *U.S.P.* 2,493,068.

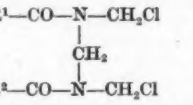
Water-repellent agents of the type—



(R^1 and R^2 = same or different hydrocarbon radicals containing an alkyl chain of > 7 C, but may be otherwise straight or branched, sat. or unsat., and may also contain aromatic or *cyclo*aliphatic radicals) are obtained by treating a long-chain aliphatic amide (or a mixture of two such amides) with dry formaldehyde in presence of an organic sulphonic acid to yield an intermediate of formula—



On treating this with hydrogen chloride, the oxadiazine ring opens up and the corresponding bischloromethyl compound—



is formed. This is treated with pyridine to obtain the final product. C. O. C.

Durable Water-repellent Finish. M. Pollock, E. Zerner, and Sun Chemical Corpn. *U.S.P.* 2,493,360.

A compound R·CN (R = an aliphatic group of 12–20 C) is treated with formaldehyde in absence of water and in presence of sulphuric or chlorosulphonic acid as catalyst, and the resulting compound treated with phosphorus trichloride. Textiles impregnated with an alkaline aqueous dispersion or solution of the above products and then dried and cured for 5 min. at 140–150°C. are rendered durably water-repellent. C. O. C.

Water-repellent Finish fast to Dry Cleaning and Laundering. E. Zerner, P. I. Pollak, and Sun Chemical Corpn. *U.S.P.* 2,489,473.

A compound of formula R·CO·NH_2 (R = alkyl of 12–30C), alone or mixed with the corresponding free fatty acid or a mixture of C_{12-30} fatty acids and their nitriles, is heated at 300–350°C. until the mixture has A.V. < 25. It is then chloromethylated, and subsequently treated with a tertiary amine. Textiles impregnated with the product and then baked at 100–180°C. are given a soft handle and a water-repellent finish which resists repeated dry cleanings or launderings. C. O. C.

Water-repellent Compositions containing Stearamide and Methylated Methylolmelamine. G. I. Cathers, L. A. Fluck, and American Cyanamid Co. *U.S.P.* 2,491,249.

Clear concentrated solutions can be obtained by heating a higher fatty acid amide with a concentrated aqueous solution of methylated methylolmelamine at not < 180°C. If a little of a dispersing agent, e.g. soap, is added to the hot solution, then upon rapid cooling the fatty acid amide is obtained in a very finely divided form. The resulting paste or suspension of amide and dispersing agent in conc. aqueous methylolmelamine is stable and shows no tendency to cream or coagulate upon storing. It is readily diluted or dispersed in water to yield textile-finishing baths. C. O. C.

Compositions for rendering Fibrous Material Water-repellent. Monsanto Chemical Co. *B.P.* 636,878.

Aqueous dispersions containing (*a*) an *NN'*-diacyldiaminomethane whose acyl groups are derived from aliphatic acids containing 12–28 C, e.g. distearamidomethane, (*b*) dimethylolurea, a dimethylolurea ether, tetramethylolmelamine, or a tetramethylolmelamine ether, the ethers being those obtained from alcohols containing 1–6 C, e.g. dibutyl ether of tetramethylolmelamine, and (*c*) a dispersing agent, e.g. ammonium oleate, when used to impregnate fibrous materials and then heat-cured, impart a water-repellent finish. C. O. C.

***iso*Cyanate Derivatives of Rosin.** S. T. Putnam and Hercules Powder Co. *U.S.P.* 2,491,580.

Rosinyl, hydrorosinyl, and dehydrorosinyl *iso*cyanates are obtained in stable form by treating an amide of the corresponding rosin acid with an alkali-metal hypohalite. They are colourless viscous liquids of b.p. approx. 160°C. at 1 mm. pressure. They are stable in cold water, but react with alcohols and amines. With cellulose they react with the OH groups to form a water-repellent coating.

and they also form such a coating on wool. They are also useful for forming the corresponding amines, which are used as emulsifying and wetting agents and as fungicides and bactericides. C. O. C.

Polymeric Polyamines—Textile Auxiliary Agents, etc., Fibres, Dye Intermediates. H. H. Hoehn and Du Pont. *U.S.P.* 2,495,255.

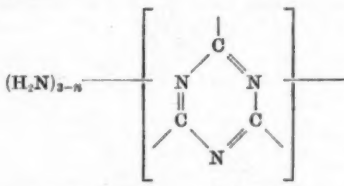
The products obtained by reduction in presence of anhydrous ammonia or primary or secondary amines of polymers of 150–1 parts of monoolefin to one part of carbon monoxide have very wide uses as auxiliary agents, e.g. as water-repellent finishes, for rendering wool non-felting, and for fixing acid dyes fast to water on cellulose. Some of them are suitable for making into fibres and films or as intermediates for oil-soluble dyes for colouring polyethylene fibres. C. O. C.

Improving the Stability of an Unstable Solution of a Reaction Product of Melamine, an Aldehyde, and a Bisulphite. Monsanto Chemical Co. *B.P.* 636,892.

The stability of an unstable aqueous solution of a reaction product of melamine, an aldehyde, and a bisulphite is improved considerably by adding to the solution a small proportion of a water-soluble hydroxide having readily dissociated hydroxyl ions, but the wet-strengthening properties conferred on paper by adding the resin to the beater are unimpaired. S. V. S.

Aldehyde–Triazine Derivative Condensates. E. L. Kropa and American Cyanamid Co. *U.S.P.* 2,496,097.

The condensates of an aldehyde and a triazine derivative of formula—



(R = a polymerisable, univalent, primary, monoethylenically unsat. aliphatic radical of 3–10 C which may be substituted by H, Cl, or univalent hydrocarbon radicals; n = 1 or 2) are resins with a very wide range of uses, e.g. in coating and moulding compositions, as textile and leather finishes, etc. C. O. C.

Flameproofing Agents. R. A. Pingree, R. C. Ackerman, and Sun Chemical Corpn. *U.S.P.* 2,488,034.

The product obtained by heating 1 mol. of guanylurea phosphate with 2–3 mol. formaldehyde at 40–100°C. until a clear, slightly viscous, colourless, water-soluble condensate is formed has excellent flameproofing properties. It can be heat-cured to an infusible, insoluble resin, curing being accelerated greatly by the incorporation of small amounts of melamine–formaldehyde resins. When used on textiles a plasticiser, e.g. stearoyloxymethylpyridinium chloride, is best incorporated in the finish. C. O. C.

Mildewproofing Agent. B. F. Goodrich Co. *B.P.* 636,459.

The products obtained by treating a 2-mercaptothiazole with formaldehyde, by the process described in *U.S.P.* 1,960,196, are used in aqueous suspension as mildewproofing agents for textiles. C. O. C.

Rotproofing Agents. M. Goll and Nuodex Products Co. Inc. *U.S.P.* 2,494,941.

A homogeneous solution of a water-insoluble copper salt of naphthenic acid and a water-soluble quaternary ammonium compound, the four valencies of whose N atom are linked to organic radicals, the anion being that of a water-soluble acid, e.g. an oil-soluble solution containing zinc naphthenate stabilised to water leaching by > 25% by weight of a metal salt of dodecyldimethylbenzylammonium chloride, is used for rotproofing textiles, etc. C. O. C.

Organic Phosphate Esters—Insecticides, Fungicides, and Plasticisers. E. I. Hoegberg and American Cyanamid Co. *U.S.P.* 2,494,126.

Compounds $X^1P(OR^2)(OR^3)\cdot X^2\cdot[CHR^1]_m\cdot CO\cdot NH\cdot CO\cdot NR^4R^5$ (X^1 and X^2 = O or S; R^1 = H or alkyl; R^2 and R^3 = alkyl, aralkyl, or aryl; R^4 and R^5 = H, alkyl, or aryl; m = a small whole number), e.g. *OO'*-diethyl *S*-ureidoformylmethyl monothiophosphate, are insecticides (e.g. toward black carpet beetles), fungicides, plasticisers, and corrosion inhibitors.

J. T. Cassaday, E. I. Hoegberg, B. D. Gleissner, and American Cyanamid Co. *U.S.P.* 2,494,283.

Compounds of formula— $X^1P(OR^1)(OR^2)\cdot X^2\cdot[CH_2]_m\cdot CX^3\cdot NR^3R^4$ (R^1 and R^2 = alkyl, aralkyl, or aryl; R^3 and R^4 = H, alkyl, hydroxyalkyl, aryl, or nitroaryl; X^1, X^2, and X^3 = O or S; m = a small whole number), e.g. *OO'*-diethyl *S*-carbamylmethyl dithiophosphate, have similar properties to the above.

U.S.P. 2,494,284.

Compounds of formula $XP(OR^1)(OR^2)\cdot S\cdot CH_2\cdot CN$ (R^1 and R^2 = alkyl or aryl; X = O or S), e.g. *S*-cyanomethyl *OO'*-diethyl dithiophosphate, have similar properties to the above. C. O. C.

Synthetic Adhesive. General Aniline & Film Corpn. and I. V. Runman. *B.P.* 635,911.

A resinous composition suitable for use as an adhesive or in varnishes is prepared by mixing a polyvinyl ether, e.g. polyvinyl *iso*butyl ether, with the resinous condensate from acetylene and a phenol, e.g. *p-tert.*-butylphenol. E. C.

Adhesive. B. J. Balfe and I.C.I. Ltd. *B.P.* 636,423.

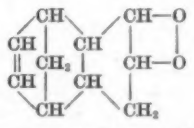
An adhesive suitable for bonding fabrics, leather, etc. is prepared by dissolving in a solvent, e.g. acetone, a modified polyesteramide as described in *B.P.* 580,524 (cf. J.S.D.C., **63**, 61 (1947)) and a resin prepared by condensing phenol or a phenolic resin with a terpene E. C.

Vinylbutyral Air-drying Wrinkle Composition. W. A. Waldie and New Wrinkle Inc. *U.S.P.* 2,494,597.

A composition which yields very uniformly wrinkled films consists of 4 lb. polyvinylbutyral, 4 gal. butanol, and 1 gal. water. C. O. C.

Oxides of Di*cyclo*pentadiene—Driers. J. H. Wells, P. J. Wilson, and Carnegie-Illinois Steel Corpn. *U.S.P.* 2,494,418.

Oxides of di*cyclo*pentadiene, e.g. di*cyclo*pentadiene peroxide—



are driers which do not continue to act after the film is dry. In addition they impart increased wetting powers to the wet film and added toughness to the dried film. C. O. C.

Chemistry and Application of Sulphonamide Resins. A. Kraus, A. Lendle, and S. A. Polaine. (XIII, p. 460.)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Production of Phenol by Direct Oxidation of Benzene. W. I. Denton, H. G. Doherty, and R. H. Krieble. *Ind. Eng. Chem.*, **42**, 777–786 (May 1950).

***N*-Methylaniline from Chlorobenzene and Methylamine.** E. C. Hughes, F. Veatch, and V. Elersich. *Ind. Eng. Chem.*, **42**, 787–790 (May 1950).

Chlorobenzene and aqueous methylamine containing a copper catalyst (e.g. cuprous or cupric chloride) are heated in a bomb reactor, and the resulting mixture is discharged through a cooling condenser to a settler, where the organic layer, which is essentially methylaniline and unchanged chlorobenzene, is separated and distilled. A flow diagram is included for a continuous process. Variables which affect the amount of conversion are time, temperature, type of catalyst, molar ratios of catalyst and methylamine to chlorobenzene, and amine concentration in water. The copper catalyst is preferably in a water-soluble form to avoid filtration and redissolution after each cycle of operation. Methylamine can be released from the hydrochloride formed in the reaction without precipitation of

catalyst, if the aqueous solution is stirred vigorously during the neutralisation. The presence of sodium chloride, due to the neutralisation process, does not affect the optimum reaction conditions. H. H. H.

Preparation of Dimethylaniline. R. N. Shreve, G. N. Vriens, and D. A. Vogel. *Ind. Eng. Chem.*, **42**, 791–796 (May 1950).

The variation in the composition of the amine mixture with time during the methylation of aniline to dimethylaniline with methanol, using a sulphuric acid catalyst, is found to be represented accurately by a first-order system; consecutive reactions, in which the rate of the first is directly proportional to the aniline concentration, and of the second to the concentration of methylaniline, have their specific rate constants equal. The variation of the reaction rate constants with catalyst concentration is represented accurately by $k = k_0 z\,(1 - 0{\cdot}5\,z)$, where z is the fraction of amine present in the form of the sulphuric acid salt. Temperatures $\sim$ 230°c. cause at least two side reactions to occur, viz. re-arrangement to nuclearly alkylated products, e.g. dimethyl-*p*-toluidine, and oxidation to formaldehyde derivatives, e.g. *pp'*-tetramethyldiaminodiphenylmethane. The reaction equilibrium becomes less favourable as the temperature is increased. The equilibrium conversion is $>$ 99% at 200°c. with 50% excess methanol. H. H. H.

Kinetics of the Condensation of Dimethylaniline with Formaldehyde. Y. Ogata and O. Okano. *J. Amer. Chem. Soc.*, **72**, 1459–1461 (April 1950).

Kinetic study of the HCl- or H_2SO_4-catalysed condensation of dimethylaniline with formaldehyde into *pp'*-tetramethyldiaminodiphenylmethane by estimating the amount of formaldehyde used up (sulphite method) shows that—(1) Formation of *p*-dimethylaminobenzyl alcohol (or -benzylcarbonium ion) is rate-determining. (2) The rate is proportional to the product of the concentrations of dimethylaniline and formaldehyde present. (3) The reaction is very slow in absence of acid, but excess acid also reduces the rate. (4) Addition of an inorganic salt, e.g. NaCl, increases the rate. C. O. C.

Sulphonation with Sulphites. XIV—Mechanism of "Oxidative" Sulphonation. S. V. Bogdanov and I. B. Migacheva. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 124–133 (Jan. 1950).

Sodium sulphite was oxidised in presence of a derivative of β-naphthol (e.g. 2:3-hydroxynaphthoic acid, 2-naphthol-7-sulphonic acid), and the yield of sulphonated product was determined. Only certain oxidising agents were effective in promoting sulphonation. They included a number of the type which oxidises sulphite to sulphate (e.g. permanganates, 1:2-naphthaquinone), and also some of those which convert sulphite mainly to dithionate (e.g. ferric chloride, copper sulphate). It is considered that a complex is formed containing ions of the oxidising agent and hydrated sulphite ions. Electron transfer then occurs within this complex; SO_3^{2-} becoming SO_3^-, and finally SO_3 (neutral). In absence of a suitable reactive substance these oxidation products may give rise to dithionate and sulphate respectively. Otherwise the SO_3-containing complex may act as a sulphonating agent, following the mechanism of the usual method of sulphonation by derivatives of sulphuric acid. A. E. S.

Caustic Fusion of Sodium 6-Methylnaphthalene-2-sulphonate. R. N. Shreve and F. R. Lloyd. *Ind. Eng. Chem.*, **42**, 811–817 (May 1950).

Interaction between Polynitro-compounds and Aromatic Hydrocarbons and Bases. X—Picric Acid and Alkylated Benzene Derivatives in Chloroform Solution. H. D. Anderson and D. L. Hammick. *J. C. S.*, 1089–1094 (April 1950).

The method of Moore, Shepherd, and Goodall (*J.C.S.*, 1447 (1931)), which depends on the change in the distribution ratio of picric acid between a solvent (chloroform) and water when an aromatic substance, immiscible in water, is added to the solvent, has been used for the comparison of the stabilities of the products of interaction of picric acid in chloroform solution, with a series of monoalkylated derivatives of benzene (*n*-alkylation from toluene to *n*-amylbenzene, branched-chain alkylation to *iso*propyl, *sec.*-butyl, and *tert.*-butyl). The results obtained from the equilibrium ("stability") constants show an alternating effect of increasing *n*-alkyl chain length; this is related to a "packing effect". The branching of the chain shows a progressive and presumably steric effect. H. H. H.

Displacement of the Substituent in *para*-Substituted Dimethylaniline during Azo Coupling. S. I. Burmistrov. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 277–283 (Feb. 1950).

para-Substituted dimethylaniline may couple with a diazonium salt with the elimination of the substituent (R). It is considered that the coupling mechanism is the same as in the case when R = H, i.e. the diazonium ion becomes attached to an electron-donating centre which carries the radical R, and the latter is then removed as R^+ by a proton acceptor, such as water or an acetate. Hence the readiness with which R is eliminated should depend on the stability of the cation R^+. For a number of substituents the degree of stability of this ion was estimated from thermodynamic data, taking the heat evolved in e.g. the reaction—

$$R{\cdot}C_6H_5(\text{gas}) + H^+(\text{g}) = R^+(\text{g}) + C_6H_6(\text{g})$$

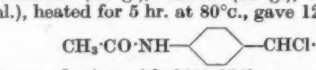
as a measure of the quantity required. Some of the above substituents occur in the 26 dimethylaniline derivatives examined experimentally. These derivatives were treated with diazotised *p*-nitroaniline and with diazotised 2:4-dinitroaniline, and the readiness with which coupling occurred was observed qualitatively. Where coupling took place the hue of the resulting azo dye indicated that the reaction was in fact at the *para* position. The results are considered to support the theory advanced. A. E. S.

Dependence of Rate of Azo Coupling of ArX on the Nature of Ar. S. I. Burmistrov. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 304–309 (Feb. 1950).

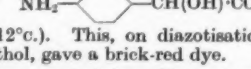
Further theoretical consideration is given to previous experimental work by the author which indicated that for a given aryl radical the rate at which ArX couples with a given diazonium salt depends on the strength of the base HX, and when this basicity is below a certain limit, ArX does not couple under the conditions used. This limiting basicity varies with the nature of Ar in much the same way as the basicity of ArX itself. It is now pointed out that the rate of coupling with ArX for a given X is related to the magnitude of the oxidation potential of the corresponding quinone $Ar'O_2$ (Ar' is the 1:2- or 1:4-arylene corresponding to Ar, according as coupling is *ortho* or *para* to X), the coupling rate being high for low values of the oxidation potential. Also, for a given X, the difference in the activation energies for the coupling reactions of any two of the compounds ArX is close to the difference in the free energy changes for the reduction reactions of the corresponding quinones to quinols. The *ortho* : *para* ratio for azo coupling may be treated on a similar basis, using thermodynamic data for the reduction reactions of 1:2- and 1:4-quinones. Calculations of this ratio are carried out in some simple cases, and the results are of the right order, but it is emphasised that in general there are steric and other factors which complicate the problem. A. E. S.

Diazotisable Base from Acetanilide and Chloral. A. Ya. Berlin, M. N. Shchukina, and E. D. Sazonova. *Zhur. Obshchey Khim.* (*J. Gen. Chem.* (*U.S.S.R.*)), **19**, 677–682 (1949): *Chem. Abs.*, **44**, 3448 (25th April 1950).

Acetanilide (24 g.), chloral (12 g.), and 98% H_2SO_4 (80 ml.), heated for 5 hr. at 80°c., gave 12 g. of—



which on refluxing with 20% HCl gave—



(m.p. 111–112°c.). This, on diazotisation and coupling with β-naphthol, gave a brick-red dye. E. S.

Monoazo Dyes containing Chromium. M. Hayaski, Y. Oshima, S. Tsuruoka, and T. Seo. *Rept. Japan. Assoen. Advancement Sci.*, **17**, 47–54 (1942): *Chem. Abs.*, **44**, 3257–3259 (10th April 1950).

Preparations of the chromium complexes of the five following monoazo compounds, and the hues of the resulting dyes, are described—4-amino-1-chloro-2-benzenesulphonic acid→salicylic acid (orange), naphthionic acid

→salicylic acid (reddish orange), 4-nitro-2-aminophenol-6-sulphonic acid→1-phenyl-3-methyl-5-pyrazolone (dark green), 6-nitro-2-aminophenol-4-sulphonic acid→1-phenyl-3-methyl-5-pyrazolone (green), and 4-chloro-2-amino-6-benzenesulphonic acid→1-phenyl-3-methyl-5-pyrazolone (dark brown).

M. Hayaski, G. Hagiyama, and T. Seo. *Ibid.*, **17**, 253–258 (1943): *Chem. Abs.*, **44**, 3259 (10th April 1950).

Similarly preparations of the chromium complexes of 6-nitro-1-amino-2-naphthol-4-sulphonic acid→1-*m*-sulphamylphenyl-3-methyl-5-pyrazolone (reddish-brown) and 1-amino-2-naphthol-4-sulphonic acid→1-*m*-sulphamylphenyl-3-methyl-5-pyrazolone (dark purple) are described. E. S.

Spectrochemical Studies of Metallic Complexes containing the Triazene [Diazoaminobenzene] Molecule. I—The Dinitrotriazenes. T. Uémura, Y. Sato, and S. Arikawa. *Bull. Chem. Soc. Japan*, **21**, 9–18 (July 1948).

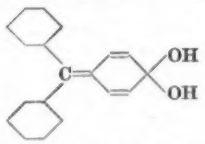
The absorption spectra of triazene and its dinitro derivatives have a principal band in the visible or near ultra-violet, and, while similar in alcoholic or acetone solution, are somewhat different in pyridine. The small absorbing power of the *oo'*-derivative is ascribed to interaction between the nitro and amino groups, which diminishes the resonance of the molecule, whereas the large value for the *pp'*-derivative indicates a stable polar quinonoid structure due to facile resonance and pronounced bathochromic effect. The *mm'*-compound, which exhibits neither a bathochromic effect nor absorbing power, cannot possess either a polar quinonoid or a stable resonance structure. Where the two nitro groups are asymmetrically oriented, then their effects are superposed. H. H. H.

Crystallisation of Congo Red. P. Mitchell. *Nature*, **165**, 772–773 (13th May 1950).

General experience has been hitherto that the benzidine disazo dyes crystallise only with difficulty, and then in company with much amorphous material. The potassium salt of Congo Red has now been precipitated in crystalline form by salting out with potassium acetate at ~ 95°c. A photomicrograph shows the crystals to be very thin, optically anisotropic plates, which in the polarising microscope exhibit red–blue optical dichroism. It would appear that a large steric factor or entropy decrease is involved in the crystallisation process, and, consequently, that rise of temperature favours the rate of formation of crystalline more than that of the amorphous material. This technique should favour the crystallisation of substances of high mol. wt. more than does the usual salting-out procedures or methods involving precipitation from aqueous solution by addition of organic solvents. H. H. H.

Hydroxyfuchsone Dyes. X—So-called Tautomerism of Hydroxytriarylcarbinols. I. S. Ioffe and Z. Ya. Khavin. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 158–170 (Jan. 1950).

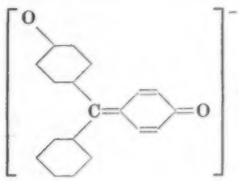
The colourless and coloured varieties of 4-hydroxytriphenylcarbinol and its derivatives were regarded by Gomberg and others as tautomers, the coloured form being e.g.—



The evidence upon which this hypothesis was based is examined critically and found to be very unsubstantial. Experiments are carried out which indicate that the coloured modifications are mixtures of the colourless carbinol and the yellow fuchsone formed by the elimination of water. The fuchsone is strongly adsorbed by the carbinol crystals, but can be removed almost completely by repeated washing with benzene, in which the fuchsone is preferentially soluble. A completely colourless carbinol can be obtained by removing the fuchsone as the bisulphite compound. In aq. acetic acid an equilibrium is established between carbinol and fuchsone; it can be approached from either side. The position of equilibrium, and also the colour and m.p. of the crystals obtained on evaporation, depend on the acetic acid concn. It is shown that the loss in wt. on heating, which was used by Gomberg as a quantitative indication of the amount of fuchsone in a preparation, is not a reliable criterion, since reactions other than simple dehydration occur. The spectroscopic evidence of Gomberg and others is found to be in accordance with the present hypothesis. A. E. S.

Hydroxyfuchsone Dyes. XI—Breakdown of Dyes of the Benzaurin Type by Alkaline Oxidation. I. S. Ioffe. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 346–355 (Feb. 1950).

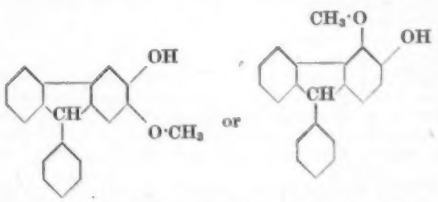
Alkaline solutions of dyes of the benzaurin type were treated with oxygen, when oxidative breakdown occurred, leading, as in the case of aurin, to the formation of a deriv. of benzophenone. The course of the reaction was followed by taking samples at intervals; these were acidified and examined colorimetrically. Contrary to experience with aurin, it was found that the rate of reaction decreased with increase of alkali concn. This arose from the much greater tendency for benzaurins to form the colourless carbinol anion in alkaline soln. It is the coloured mesomeric anion, e.g.—



which is subject to oxidation; the undissociated hydroxyquinone form and the carbinol anion are stable. As the alkalinity is increased, the rate of oxidation of the coloured anion increases as in the case of aurin, but this is more than offset by the reduction in the equilibrium concn. of the active form, which results from the increased alkalinity. The oxidation product from 3:3′-dimethoxybenzaurin, viz. 3-methoxy-4-hydroxybenzophenone, has not been described previously. It has a m.p. of 97–98°c. It follows that the already known methoxyhydroxybenzophenone of m.p. 131–132°c., obtained from guaiacol and benzoyl chloride, is the 4:3-derivative. A. E. S.

Hydroxyfuchsone Dyes. XII—Effect of Acids on Derivatives of Methoxyfuchsone. I. S. Ioffe. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 539–549 (March 1950).

In the course of the previous investigation in this series (see above), it was found that, on heating with mineral acid, 3:3′-dimethoxybenzaurin yields a colourless substance which does not react with bisulphite and dissolves in alkali without giving the characteristic blue colour of the dye. The same reaction is given by 3-methoxyfuchsone and 3:3′:3″-trimethoxyaurin, but not by fuchsone derivatives which do not contain a methoxyl group. The substances formed have in all cases the same empirical formula and mol. wt. as the original fuchsone derivative. A study of the effect of acid concn. on the reaction rate leads to the conclusion that the reactive species is the coloured oxonium cation. When a methoxyl group is present in the *ortho* position to the oxonium centre, an intramolecular isomeric change occurs, and this is considered to involve the linking of two benzene rings through their 2- or 6-positions with the formation of a 9-phenylfluorene derivative, e.g. from 3-methoxyfuchsone—



The properties of these substances and their acetyl derivatives are described, but the precise orientation of their substituents was not determined. A. E. S.

Azomethine Dyes from 4-Arylazo-5-pyrazolones. P. W. Vittum, G. W. Sawdey, R. A. Herdle, and M. K. Scholl. *J. Amer. Chem. Soc.*, **72**, 1533–1536 (April 1950).

4-Arylazo derivatives of pyrazolones undergo oxidative condensation with *NN*-disubstituted *p*-phenylenediamine to yield magenta azomethine dyes. These reactions involve replacing the 4-arylazo group by the *p*-phenylenediamine residue, the azomethine dye in every case being identical with that formed from the parent pyrazolone complex. C. O. C.

Reaction between Pyrazolones and their Azomethine Dyes. P. W. Vittum and F. C. Duennebier. *J. Amer. Chem. Soc.*, **72**, 1536–1538 (April 1950).

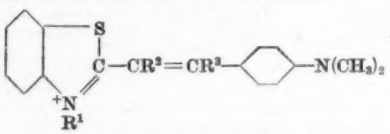
1-Phenyl-3-alkyl- or -acylamido-5-pyrazolones rapidly decolorise the azomethine dyes derived from them to yield 4:4′-bispyrazolone derivatives. C. O. C.

Colour of Organic Dyes and the Planarity of their Molecules—I. A. I. Kiprianov and I. K. Ushenko. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 134–144 (Jan. 1950).

Thiocyanine and thiocarbocyanine dyes, containing large, closely situated groups (*N*-substituents and substituents in the polymethin chain) in their molecules, are compared with the corresponding unsubstituted dyes. Their absorption bands are displaced towards the red, and it is considered that the steric effect of the substituents disturbs the coplanarity of the heterocyclic nuclei and leads to a reduction in the resonance effect, and hence in the separation of the excited and ground states of the molecule. The m.p. of a non-planar dye is higher, and its solubility in alcohol lower, than those of the corresponding planar dye. The syntheses of 15 new thiocyanine dyes are described. A. E. S.

Colour of Organic Dyes and the Planarity of their Molecules—II. A. I. Kiprianov and I. K. Ushenko. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 514–517 (March 1950).

The considerations which were applied to the dyes studied in the first paper of this series (see above) are valid only when the dye molecule possesses a high degree of symmetry; otherwise the energy differences between the resonance structures may be considerable, and the degree of resonance low. For dyes of low symmetry the displacement of the absorption spectrum, following the introduction of groups which disturb the flatness of the conjugated system, may be towards the *short* waves, and this is found to be the case for dyes of the general formula—



($R^1 = C_6H_5$ or C_2H_5; and R^2, R^3 = H or a hydrocarbon radical). The hypsochromic effect is accompanied by a considerable reduction in the absorption intensity; e.g. for $R^1 = C_2H_5$ and $R^2 = R^3 = H$, $\lambda_{max} = 530$ mμ. and $\varepsilon_{max} = 11{\cdot}0 \times 10^4$; for $R^1 = C_2H_5$, $R^2 = CH_3$, and $R^3 = H$, $\lambda_{max} = 481$ mμ. and $\varepsilon_{max} = 6{\cdot}2 \times 10^4$. The syntheses of a number of new dyes of the above type are described. A. E. S.

Chemistry of Photographic Sensitising Dyestuffs. J. D. Kendall. *Chem. and Ind.*, 121–124 (18th Feb. 1950).

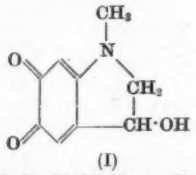
The development of photographic sensitisers is described historically and the relation between the different types is formulated. Sensitising systems consist of a cationoid organic component joined to an anionoid component by a simple conjugated double-bond system absorbing at the appropriate wavelength. Desensitisers consist of such a system with two cationoid components, and in developing systems two anionoid components are connected by the conjugated double-bond chain. What determines the magnitude of the effect is not known. W. J. M.

Chemistry of Gamboge. M. Land and A. Katz. *Pharm. Acta Helv.*, **24**, 387–401 (1949): *Chem. Abs.*, **44**, 3214 (10th April 1950).

From gamboge, acetyl-α-gambogic acid is prepared. When treated with aqueous-alcoholic KOH at 175°C. in an autoclave 2-methyl-2-hepten-6-ol is produced. The amorphous ether-soluble acids arising from the degradation produced after methylation and oxidation with $KMnO_4$ yield phthalic acid, an acid $C_{12}H_{16}O_9$, m.p. 286°C. (dimethyl ester m.p. 164°C.), and an acid, m.p. 180°C. A substance, which was a phenol or a weak acid, $C_{16}H_{28}O_{27}$ m.p. 294°C. (monomethyl derivative m.p. 228°C.) was isolated. C. O. C.

Chemistry of Adrenochrome and its Derivatives. J. Harley-Mason. *J.C.S.*, 1276–1282 (May 1950).

The reduction of adrenochrome (I) gives rise to 5:6-dihydroxy-1-methylindole and an intermediate zwitterion which is easily converted into 3:5:6-trihydroxy-1-methylindole. The latter is also obtained by the action of alkali on (I), and on oxidation gives 5:6:5′:6′-tetrahydroxy-1:1′-dimethylindigo. The conversion of (I) into "adrenaline black" is described, and the structure of the latter is discussed. The preparation of aqueous solutions of (I) by oxidation of adrenaline with buffered persulphate is described.



(I) H. H. H.

Chrome–Tin Pink. H. N. Bose. *Trans. Indian Ceram. Soc.*, **7**, 28–31 (1948): *Chem. Abs.*, **44**, 3228 (10th April 1950).

A satisfactory composition for an underglaze pink stain was— CaO 23·32, SnO_2 31·48, SiO_2 41·64, PbO 2·69, Cr_2O_3 0·9%. C. O. C.

Zinc Yellow. B. Dowarah and H. N. Bose. *J. & Proc. Inst. Chemists* (India), **21**, (3), 91–96 (1949): *Chem. Abs.*, **44**, 3720 (25th April 1950).

A good yield of zinc chrome yellow with a slight greenish cast is obtained with 50 g. ZnO (White Seal Grade, 20% slurry), 5 ml. H_2SO_4 (sp. gr. 1·5, 10% strength), and 55 g. $K_2Cr_2O_7$ (20% solution). The acid is added to the ZnO slurry, and the temperature raised to 50°C.; the $K_2Cr_2O_7$ solution at 50°C. is then added, and the whole uniformly agitated until the reaction is completed. This temperature results in the finest precipitate. To obtain a greenish cast slight excess of $K_2Cr_2O_7$ over the above is used. C. O. C.

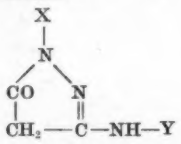
Temperature of Zero Conductance of Certain Dyes. S. Prakash and T. N. Shivapuri. *Current Sci.* (India), **18**, 403, 404 (1949): *Chem. Abs.*, **44**, 3713 (25th April 1950).

The temperature of zero conductance of Methylene Blue, Fuchsin, Aniline Blue, Indigocarmine, Bordeaux B, Benzopurpurin, Congo Red, Aniline Brown, Methyl Orange, Dianil Azurin G, and Aniline Scarlet is between − 21·0 and − 23·5°C. The temperature of zero conductance is higher for solutions containing colloidal micelles than for those containing ordinary electrolytes. C. O. C.

PATENTS

Photographic Colour Couplers. Gevaert Photo-Producten N. V. and J. J. Jennen. *B.P.* 636,988.

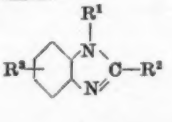
Compounds of formula—



(X = H, alkyl, aryl, acyl, or a heterocyclic radical; Y = a heterocyclic radical) are used as photographic colour couplers. C. O. C.

Cyan Colour Formers. General Aniline & Film Corpn. and W. C. Craig. *B.P.* 636,996.

Compounds of formula—



(R^1 = a long-chain aliphatic radical; R^2 = a hydroxy-aromatic radical, the OH group being attached to a nucleus linked to the benziminazole radical *ortho* to the OH group; R^3 = a water-solubilising group), e.g. 1-octadecyl-2-α-hydroxy-β-naphthylbenziminazole-5-sulphonic acid, yield cyan dye images of exceedingly fine grain when developed with a *p*-phenylenediamine developer. C. O. C.

Quaternising Agents for Heterocyclic Nitrogenous Cyanine Dye Intermediates. General Aniline & Film Corpn. and A. W. Anish. *B.P.* 636,906.

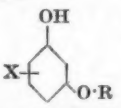
Introduction of one or two methylene groups between a *p*-toluenesulphonate group and a nitrogenous heterocyclic system produces compounds (substituted methyl or ethyl esters) which, when used as alkylating or quaternising agents for basic nitrogenous heterocyclic dye intermediates, yield dye salt intermediates which undergo the usual reactions for preparing cyanine dyes. C. O. C.

Stabilisers for Diazotype Compositions. General Aniline & Film Corpn. and S. C. Slifkin. *B.P.* 635,533 and *U.S.P.* 2,495,827.

Compounds of formula R·CH:C(COOH)·$[CH_2]_n$·COOH (R = H, alkyl, aralkyl, or aryl; n = 1–4), e.g. itaconic or α-methyleneglutaric acid, are good stabilisers for light-sensitive diazo compounds and also prevent premature coupling of diazotype compositions. C. O. C.

Resorcinol Monoethers as Coupling Components in Diazotype Layers. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *B.P.* 636,761.

Compounds of formula—



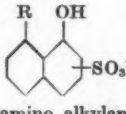
(R = alkyl, *cyclo*alkyl, aryl, or aralkyl radical, which may be substituted by halogen, hydrogen, alkoxy, carboxy, carboalkoxy, sulpho, or amino; X = H, alkyl, halogen, carboxy, alkoxy, hydroxyalkyl, aryl, alkaryl, aralkyl, carboalkoxy, carbamido, or –CH·NY·Y; Y's = same or different H, alkyl, hydroxyalkyl, aryl, alkaryl, aralkyl or *cyclo*alkyl, or may be joined to complete a heterocyclic ring) are highly stable to precoupling and yield dense sepia images. C. O. C.

Resorcinolcarboxyamides as Coupling Components in Diazotype Compositions. General Aniline & Film Corpn. and F. W. Neumann. *B.P.* 636,891.

Amides of resorcinolmonocarboxylic acids when used as coupling components in diazotype compositions yield maroon prints of excellent fastness to washing on a light background. They are also stable to precoupling. C. O. C.

Cyan Component for Diazotype Compositions. S. C. Slifkin, T. J. Trojnar, and General Aniline & Film Corpn. *U.S.P.* 2,494,906.

Compounds of formula—



(R = OH, NH_2, acylamino, alkylamino, or arylamino), e.g. 1:8-dihydroxynaphthalene-4-sulphonic acid, are used as coupling components in diazotype compositions to yield blue-greens. C. O. C.

***N*-Acyl-*N*-arylhydrazines as Azo Dye Components.** W. E. Handford and General Aniline & Film Corpn. *U.S.P.* 2,495,000.

Azo dyes are formed by treating the usual colour photography coupling components with *N*-acyl-*N*-arylhydrazines. C. O. C.

Readily Dispersible Azoic Bases. F. Dawson, J. Swaine, W. Todd, H. Wakefield, E. R. Wiltshire, and I.C.I. Ltd. *B.P.* 635,600.

Amines or their salts which have low solubility in water (e.g. 4-amino-3-nitrotoluene) are rendered more readily diazotisable by admixture with a dispersing agent (e.g. a condensate of 2 mol. of naphthalene-2-sulphonic acid and formaldehyde), followed by grinding to a particle size of $< 50\mu$. E. S.

Metallised Monoazo Dyes for Lacquers, Nylon, etc. Ciba Ltd. *B.P.* 637,404.

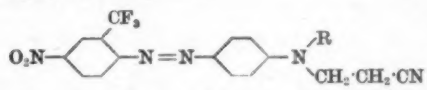
The metallisation of *oo'*-dihydroxyazo dyes free from sulpho and carboxy groups is accomplished by heating with a solution containing the metal (e.g. chromium) in complex union with an aromatic *o*-hydroxycarboxylic acid (e.g. salicylic acid). The dyes so formed may be used for colouring lacquers, etc. or for dyeing superpolyamide fibres. Thus, the monoazo compound 4-nitro-2-aminophenol→acetoacetanilide is refluxed with a solution of potassium sodium chromosalicylate, so that the resulting complex contains 1 atom of Cr to 2 mol. of monoazo compound. It dissolves in cellulose nitrate lacquer with a greenish-yellow colour. E. S.

Monoazo Chrome Dyes. Ciba Ltd. *B.P.* 636,681.

Monoazo metachrome dyes are made by treating *oo'*-dihydroxymonoazo dyes containing a single sulpho group with an acylating agent free from solubilising groups. Thus, the monoazo compound 1-amino-2-naphthol-4-sulphonic acid→β-naphthol is treated in dry pyridine with benzoyl chloride to yield a blue metachrome dye. During dyeing, the acyl residue is eliminated with formation of the chromium complex of the *oo'*-dihydroxy compound. E. S.

***p*-Nitro-*o*-trifluoromethylbenzeneazo-*N*-β-cyanoethyl-*N*-hydroxyalkylanilines — Scarlet Dyes for Cellulose Acetate.** J. B. Dickey and Eastman Kodak Co. *U.S.P.* 2,492,972.

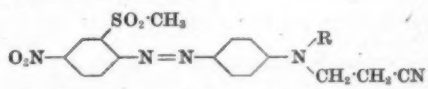
Compounds of formula—



(R = β-hydroxyethyl or β- or γ-hydroxypropyl) dye cellulose acetate scarlet with exceptional fastness to light and gas fading. C. O. C.

***p*-Nitro-*o*-methylsulphonylbenzeneazo-*N*-β-cyanoethyl-*N*-hydroxyalkylanilines — Red Dyes for Acetate Rayon.** J. B. Dickey and Eastman Kodak Co. *U.S.P.* 2,492,971.

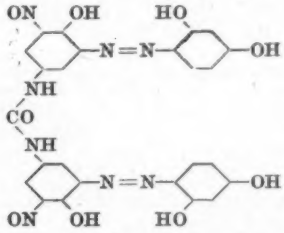
Compounds of formula—



(R = β-hydroxyethyl or β- or γ-hydroxypropyl) dye cellulose acetate red with exceptional fastness to light and gas fading. C. O. C.

Brown, Metalliferous Azoic Dyes. J. Miller, E. A. Markush, and Pharma Chemical Corpn. *U.S.P.* 2,491,928.

A coupling component for brown azoic dyeings is made by treating 4:4'-dihydroxy-3:3'-diaminodiphenylurea with nitrous acid, to form the dinitrosotetrazo compound, and coupling with 2 mol. of resorcinol, giving—



This disazo compound couples on the fibre with diazo compounds, e.g. diazotised *o*-aminodiphenyl, in presence of metallic salts, e.g. sodium chromate, to give metallised azoic browns. E. S.

Blue, Substantive Disazo Dye. H. H. Bestehorn, C. H. Stratton, and General Aniline & Film Corpn. *B.P.* 636,771.

A greenish-blue substantive dye whose good light fastness is not reduced by crease-resisting finishes is made by

treating the disazo compound 1-amino-8-naphthol-4:6-disulphonic acid ← dianisidine → 1-amino-8-naphthol-2:4-disulphonic acid with e.g. ammoniacal copper sulphate, so that the methoxy groups are eliminated with formation of a copper complex. E. S.

Disazo Dyes from 3 : 3′-Dihydroxy-4 : 4′-diaminodiphenyl. Ciba Ltd. *B.P.* 635,621.

as-Disazo dyes are made by coupling tetrazotised 3:3′-dihydroxy-4:4′-diaminodiphenyl with two different coupling components, the second coupling being carried out under more alkaline conditions than the first. Thus, by coupling first with 1 mol. of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone in presence of dilute acetic acid, and then with 1 mol. of 3-methyl-5-pyrazolone in presence of caustic soda and soda ash, an aftercoppering bordeaux dye for cotton is formed. E. S.

Acid Dyes from 2 : 4-Dichloro-1-aminoanthraquinone. S. G. Bedekar and K. Venkataraman. *B.P.* 634,645.

Blue acid dyes are prepared by condensing 2:4-dichloro-1-aminoanthraquinone with a primary or secondary aliphatic or aromatic amine, e.g. *p*-toluidine, in a boiling solvent, e.g. amyl alcohol, in presence of an acid binder, e.g. sodium acetate, and copper or one of its salts, and sulphonating the product.

B.P. 634,646.

2:4-Dichloro-1-aminoanthraquinone is made by passing dry chlorine into a suspension of 1-aminoanthraquinone in glacial acetic acid at 90–100°c. R. K. F.

Anthraquinone–Acridones. H. Z. Lecher, W. S. Forster, and American Cyanamid Co. *U.S.P.* 2,492,802.

Improved yields and purities of the acridone derivative are obtained by cyclising the corresponding arylaminoanthraquinone- or anthrimide-*o*-carboxylic acid in two stages— (i) heat at approx. 80°c. with thionyl chloride and (ii) add a small amount of phosphorus oxychloride. Thus, all parts being by weight, 1-*o*-carboxyanilinoanthraquinone (25) is heated for 3 hr. at 80–90°c. in nitrobenzene (90) containing thionyl chloride (9·8). Phosphorus oxychloride (1·7) is added, and the mixture heated to reflux. The acridone separates on cooling. R. K. F.

Chrysoidine–Basic Dye Complexes. R. C. Locke and Du Pont. *U.S.P.* 2,492,163.

A water solution of Chrysoidine is mixed at about 80°c. with a solution of one or more basic dyes of the polyarylmethane, ketonimine, xanthen, acridine, or thiazole classes containing neither sulpho nor carboxyl groups. One of these basic dyes is Crystal Violet and the amounts used are such that there is 1 mol. of Chrysoidine for each mol. of other basic dye. The resulting complexes, which separate on cooling, are black colouring matters having better properties than ordinary mixtures of basic dyes for making printing inks, carbon papers, etc. R. K. F.

Thioindigo Pigments. D. B. Killian and Du Pont. *U.S.P.* 2,493,072.

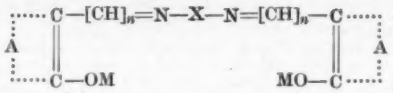
Thioindigo pigments, prepared by cyclising a phenylthioglycollic acid in e.g. oleum, have improved tinctorial properties if the reaction occurs in presence of an organic thiol. Thus, all parts being by weight, *n*-dodecyl thiol (5) in carbon tetrachloride (80) is added to chlorosulphonic acid (315) at 0–5°c. 2-Methyl-4-chlorophenylthioglycollic acid (100) is added, and the reaction continued for 3 hr. at a final temperature of 20°c. The resulting maroon pigment is separated by pouring into water. R. K. F.

Hydroxyalkylamine Salts of Sulphonated Copper Phthalocyanine— Pigments. J. Paige and General Aniline and Film Corpn. *U.S.P.* 2,490,704.

Pigments for lacquers and varnishes are made by adding an *NN*-dialkylpolymethyleneolamine, e.g. *NN*-bis-2-ethylhexylethanolamine, to an aqueous solution of a sulphonated copper phthalocyanine, and filtering off the resulting precipitate. Where the amine is insoluble in water, it is added as a salt, e.g. of phosphoric acid. R. K. F.

Azanol Dyes. General Aniline & Film Corpn., A. W. Anish, and L. C. Hensley. *B.P.* 637,450.

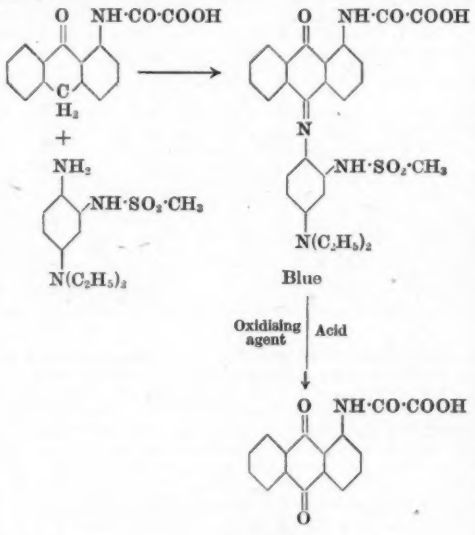
Azanol dyes of formula—



(A = atoms necessary to complete a 5- or 6-membered heterocyclic ring, M = H or a heavy metal, n = 1 or 3, N·X·N = a radical of hydrazine or an aliphatic, aromatic, or heterocyclic diamine containing two primary amino groups and < 15 C) are obtained by condensing a 5- or 6-membered heterocyclic keto compound, containing a reactive group, with an aliphatic, aromatic, or heterocyclic diamine while heating in presence of an alcohol and, if desired, a tertiary base. They are soluble in aqueous solutions of inorganic bases and form stable heavy-metal salts. They are used as sensitisers and filters in photography. C. O. C.

Quinoneimine and Quinone Dyes. General Aniline & Film Corpn., W. A. Schmidt, V. Tulagin, and M. E. Chiddix. *B. P.* 637,093.

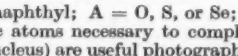
Quinoneimine dyes more stable than those hitherto produced are obtained by using a 9-hydroxy- or 9-aminoanthracene as the colour former (the OH may be esterified). They are converted into very stable quinone dyes by treatment with acid in presence of an oxidising agent. An example is—



C. O. C.

***mero*Cyanine and Rhodacyanine Dyes.** General Aniline & Film Corpn. and A. W. Anish. *B.P.* 636,738.

*mero*Cyanine and rhodacyanine dyes containing a heterocyclic nucleus of formula—



(R = phenyl or naphthyl; A = O, S, or Se; m = 2 or 3; X = non-metallic atoms necessary to complete a heterocyclic nitrogen nucleus) are useful photographic sensitisers. Methods of making them are described. C. O. C.

Acid *mero*Cyanine Dyes. L. G. S. Brooker, F. L. White, and Eastman Kodak Co. *U.S.P.* 2,493,747.

*mero*Cyanine dyes containing in the keto nucleus at least one sulpho or carboxyl group have in many cases a weaker photographically sensitising action than the *mero*cyanine dyes hitherto known but have the advantage that they leave less permanent stain. C. O. C.

Acid *mero*Cyanine Dyes. L. G. S. Brooker, G. H. Keyes, and Eastman Kodak Co. *U.S.P.* 2,493,748.

*mero*Cyanine dyes containing in the keto nucleus sulphoalkyl and/or carboxyalkyl groups have similar properties to those described in *U.S.P.* 2,493,747 (above). C. O. C.

Dimethin *mero*Cyanine Dyes. L. G. S. Brooker, F. L. White, and Eastman Kodak Co. *U.S.P.* 2,494,031.

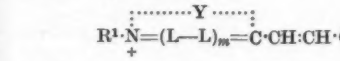
Dimethin *mero*cyanine dyes containing an alkoxy or aryloxy group on the methin group furthest from the keto nucleus are photographic sensitisers. C. O. C.

Polymethin Dyes. Kodak Ltd. and V. P. Pittman. *B.P.* 637,039.

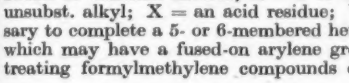
Polymethin dyes are prepared by condensing a *cyclo*ammonium quaternary salt having a CH_3 group attached to the C atom α or γ to the quaternary N atom, e.g. 2-methylthiazole ethiodide, with a compound of formula O:CH·CHal:C(O·R)·COOH (R = H, methyl, ethyl, or phenyl) in presence of a tertiary organic base having a dissociation constant greater than that of pyridine. C. O. C.

Polymethin Dyes and their Intermediates. Gevaert Photo-Producten N.V. *B.P.* 637,815.

The products of formula—



(R^1 = subst. or unsubst. alkyl, aryl, or alkylene; L = subst. or unsubst. methin; $m = 0$ or 1; R^2 = subst. or unsubst. alkyl; X = an acid residue; Y = atoms necessary to complete a 5- or 6-membered heterocyclic nucleus, which may have a fused-on arylene group), obtained by treating formylmethylene compounds of formula—



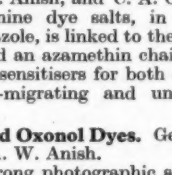
with quaternating agents of formula R^2X, yield polymethin dyes when treated with heterocyclic compounds containing a reactive methyl or methylene group. C. O. C.

Trinuclear Cyanine Dyes. General Aniline & Film Corpn., A. W. Anish, and C. A. Clark. *B.P.* 637,387.

Trinuclear cyanine dye salts, in which the central nucleus, di- or triazole, is linked to the other two nuclei by both a methin and an azamethin chain, are water-soluble and are excellent sensitisers for both ordinary and colour films, being non-migrating and unaffected by colour components. C. O. C.

***mero*Cyanine and Oxonol Dyes.** General Aniline & Film Corpn. and A. W. Anish. *B.P.* 637,648.

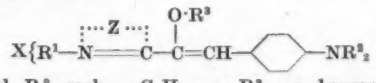
Dyes having strong photographic sensitising properties and also useful for dyeing textiles can be prepared by condensing compounds of formula—



(Z = non-metallic atoms necessary to complete a heterocyclic nucleus) with a heterocyclic nitrogen compound containing a reactive group. C. O. C.

Styryl Dyes. L. G. S. Brooker, F. L. White, and Eastman Kodak Co. *U.S.P.* 2,494,032.

Dyes of formula—



(R^1 and R^2 each = C_nH_{2n+1}; R^3 = a benzenoid or naphthenoid aryl group; X = an anion; Z = the atoms needed to complete a benzoxazole, benzothiazole, benzoselenazole, α- or β-naphthoxazole, or α- or β-naphthothiazole nucleus) have little or no photosensitising power. They are obtained by condensing a *p*-dialkylaminobenzaldehyde with an appropriate quaternary *cyclo*ammonium salt. C. O. C.

Spirit-soluble Dyes. J. Paige and General Aniline & Film Corpn. *U.S.P.* 2,490,703.

Colouring matters for lacquers, varnishes, etc. are made by combining dyes containing at least one acidic salt-forming group (e.g. sulpho or carboxylic) with an amine $(C_4H_9)_2N{\cdot}[CH_2]_n{\cdot}OH$ ($n > 1$). Thus, an aqueous solution of the dye *p*-aminoazobenzenesulphonic acid→2-benzoyl-5-naphthol-7-sulphonic acid reacts with excess *NN*-di-*n*-butylethanolamine dissolved in phosphoric acid to yield a red spirit-soluble dye. E. S.

Zirconium Lakes of Basic Dyes for Use in Printing Inks. W. B. Blumenthal and National Lead Co. *U.S.P.* 2,492,959.

Insoluble pigments are produced by treating an aqueous solution of a basic dye at pH 3·5–6·5 with a hydrous zirconia hydrogel whose usual positive charge has been changed to a negative charge by selective combination of an anion, e.g. citrate or salicylate, which induces cataphoretic movement of the resulting negative micelle to the positive electrode of a cataphoretic cell. The products are particularly suitable for use in printing inks to produce prints of unusually intense and brilliant tone. C. O. C.

Electrolytic Production of Powdered Stainless Steel, Nickel, Chromium, Copper, and other Heavy Metals. E. H. E. Johansson and C. M. Truedsson. *B.P.* 637,714.

Lead Sulphate–Silica Pigment. National Lead Co. *B.P.* 637,304.

A lead sulphate–silica pigment of superior weathering quality and good tinting strength, which is fast to light, is obtained by mixing PbO (at least partly converted to $PbSO_4$) with SiO_2, the amounts of PbO, SO_3, and SiO_2 analytically present being in proportions represented by points lying within that area of a triangular PbO–SO_3–SiO_2 composition diagram which is bounded by straight lines joining in series the four points— 72 PbO : 1 SO_3 : 66 SiO_2, 31 PbO : 6 SO_3 : 63 SiO_2, 72 PbO : 13 SO_3 : 15 SiO_2, and 77 PbO : 3 SO_3 : 20 SiO_2— the mixture being heated at 400–700°C. for 1–3 hr. C. O. C.

Rutile Titanium Dioxide of Exceptional Hiding Power and Tinting Strength. L. E. Ross, C. A. Tanner, and American Cyanamid Co. *U.S.P.* 2,494,492.

Rutile conversion is obtained much more effectively by using a rutile seed prepared by treating an alkali-metal titanate with a monobasic acid, e.g. HCl. C. O. C.

Polymeric Polyamines— Textile Auxiliary Agents, etc., Fibres, Dye Intermediates. H. H. Hoehn and Du Pont. (III, p. 447.)

V— PAINTS; ENAMELS; INKS

Pentaerythritol–Tall Oil Esters. A Review of their Preparation and Use in Surface Coatings. S. Gourley. *J. Oil & Col. Chem. Assocn.*, **33**, 175–179 (April 1950).

Pentaerythritol–tall oil esters are a useful substitute for orthodox drying oils, but their use appears to be limited by their slower rate of drying and inferior durability. There are 32 references. C. O. C.

Printed Circuits [Conductive Printing Inks]. P. B. Hopf. *Paint*, **20**, 170–172, 182 (May 1950).

The production of printed circuits by screen and offset printing is discussed, with particular reference to the properties required of the conductive inks used. C. O. C.

PATENTS

Synthetic Resin Coating Compositions having a Polychromatic or Metallic Appearance. L. V. K. Odsal, R. E. Pike, and Du Pont. *U.S.P.* 2,493,020.

A coating composition, which when sprayed produces a polychromatic or metallic finish which is uniform and free from mottling, flooding, or sagging, comprises an oil-modified alkyd resin vehicle, aluminium flakes, and a β-dialkylaminoalkylmethacrylate polymer. When the acrylate polymer is highly polymerised, then the amount present must fall within the range of the double curve represented by 0·1–0·75% on the alkyd resin, when moderately polymerised 0·25–5%, and when it has a low degree of polymerisation at least 0·4%. Pigments, etc. may also be present. C. O. C.

Bright Blue to Bluish-green Quick-drying Writing Inks. R. L. Mayhew and General Aniline & Film Corpn. *U.S.P.* 2,493,724.

A quick-drying writing ink comprises in solution a copper phthalocyanine of the benzene series having more

than one aliphatic sulphonamide group attached to the phenylene nuclei, a hygroscopic polyhydric alcohol, water, and caustic alkali equivalent to 0·5–2·0% of sodium hydroxide. C. O. C.

Setting Printing Inks with Sulphur Dichloride. Meyercord Co. *B.P.* 635,747.

Inks containing drying, semi-drying, or certain non-drying oils, e.g. olive, arachis, or castor oil, are rapidly hardened if exposed to sulphur dichloride. Materials printed with such inks can be stacked or wound immediately after exposure for < 20 sec. to sulphur dichloride vapours without any danger of offsetting occurring. Suitable apparatus is described. C. O. C.

Zirconium Lakes of Basic Dyes for Use in Printing Inks. W. B. Blumenthal and National Lead Co. (IV, p. 453.)

Azoguanamines— Components for Coloured Resins. J. T. Thurston, D. W. Kaiser, and American Cyanamid Co. (XIII, p. 460.)

Evaluation of Red Lead Pigments. III— Autocatalysis in Paint Sedimentation. IV— Improvement of Dispersion Stability of the Paints. A. Jogarao. (XIV, p. 461.)

VI— FIBRES; YARNS; FABRICS

X-Ray Research into the Structure of Cellulose Fibres. W. Kast. *Melliand Textilber.*, **31**, 83–88 (Feb. 1950).

The micellar structure of both native cellulose and a hydrated cellulose formed when native cellulose is subjected to mercerisation, solution, spinning, precipitation, and regeneration is described in terms of unit cell, space grouping, and the complete crystalline model. H. K.

Solubility of Cellulose in Strong Electrolytes, particularly Sodium Zincate. K. Borgin. *Norsk Skogindustri*, **3**, 96–103 (1949): *Chem. Abs.*, **44**, 3249 (10th April 1950).

Use of radioactive Zn in sodium zincate with ordinary tracer technique has shown that the compound of cellulose with sodium zincate which produces solubility is neither homopolar nor ionic but is held together by hydrogen bonds or dipole–dipole forces. Present opinions of the mechanism of the dissolution of cellulose in other solvents are briefly reviewed. C. O. C.

Association of Xylan with α-Cellulose in Jute. P. B. Sarkar, A. K. Mazumdar, and K. B. Pal. *Nature*, **165**, 897–898 (3rd June 1950).

α-Cellulose is hydrolysed with sulphuric acid, which is then neutralised with barium carbonate. The concentrated filtrate is subjected to paper chromatography with *n*-butyl alcohol, acetic acid, and water as solvent, using glucose and xylose as reference sugars. It is shown that no xylose is present in the chromatogram, and hence concluded that xylan is not present in α-cellulose from jute. J. W. B.

Reaction of Oxidising Agents with Wool. I— Division of Cystine into Two Fractions of Widely Differing Reactivities. P. Alexander, R. F. Hudson, and M. Fox. *Biochem. J.*, **46**, 27–32 (Jan. 1950).

When wool is treated with hypochlorite solutions at pH 2, 4, and 6 and 25°c., the cystine is almost completely oxidised. At pH 10 only 25–30% of the cystine is oxidised, even at 80°c., the excess chlorine being used up in non-cystine reactions. It appears that both free chlorine and hypochlorous acid can oxidise the cystine completely, whereas the hypochlorite ion can oxidise only 25%. The portion of the cystine which is oxidised by the hypochlorite ion is the first portion to react during acid chlorination. Acid permanganate oxidises only the same portion as this hypochlorite ion. Peracetic acid oxidises all the cystine, but the last 25% is oxidised only slowly. The difference in reactivity of the two cystine fractions cannot be ascribed to morphological causes, since the cystine of physically modified wools and powdered horn shows the same division. The two fractions are not related to the Phillips fractions (*Fibrous Proteins Symposium*, p. 39). F. F. E.

Peptides of Cystine in Partial Hydrolysates of Wool. R. Consden and A. H. Gordon. *Biochem. J.*, **46**, 8–20 (Jan. 1950).

Thirteen dipeptides of cystine in partial hydrolysates of wool have been separated and identified by means of two-dimensional chromatography on paper. It is concluded that, in wool, most of the monoamino-monocarboxylic acids are combined through both their amino and carboxyl groups to cystine residues. Evidence for the formation of intermediate oxidation products of combined cystine by the action of hydrogen peroxide has been obtained. F. F. E.

Osmotic Pressure, Molecular Weight, and Viscosity of Sodium Alginate. F. G. Donnan and R. C. Rose. *Canadian J. Res.*, **28 B**, 105–113 (March 1950).

The molecular weight of sodium alginate is determined by measurement of the osmotic pressure Π in the presence of low concentrations of sodium chloride, and extrapolation of Π/C to $C = 0$, where C is the concentration of sodium alginate. For different samples of sodium alginate, the slope of the curve Π/C against C was independent of mol. wt. If each concentration of sodium chloride is regarded as a different solvent, this work is comparable with similar work on cellulose nitrate and acetate and on polyvinyl acetate. Mean molecular weights between 48,000 and 186,000 were obtained, representing degrees of polymerisation of 220–860 sodium mannuronate units. The intrinsic viscosities of the different samples were linearly related to the degree of polymerisation. H. H. H.

Influence of Molecular Structure on the Swelling of Textile Fibres. I— N. J. Abbott. **II—** L. Rose. *J. Textile Inst.*, **41**, T 53–T 55 (Jan.–Feb. 1950).

I— Data on the swelling of drawn and undrawn nylon are presented which are in disagreement with the normally expected swelling of oriented and unoriented fibres. Present theory maintains that with a highly oriented fibre the transverse swelling is great but the axial swelling small. Unoriented fibres, on the other hand, show greater longitudinal swelling. Since X-ray diffraction patterns show drawn nylon to have a highly oriented structure and undrawn nylon to have an unoriented structure, it might be expected that undrawn nylon would have a longitudinal swelling approx. equal to the lateral swelling. The data presented show, however, that this ratio is 3 : 6. The possible explanation is given that configurations other than the crystallites must block entry of water molecules, and that it cannot be assumed that the whole amorphous region is accessible to water.

II— In a reply to N. J. Abbott it is observed that the magnitude of total swelling is small and that the ratio between lateral and longitudinal swelling is not constant over the whole range of swelling values. The difficulties in determining exactly the crystallinity by both X-ray and swelling techniques are indicated. H. K.

Magnetic Anisotropy of Dimethyl Terephthalate and Polyethylene Terephthalate. P. W. Selwood, J. A. Parodi, and A. Pace. *J. Amer. Chem. Soc.*, **72**, 1269–1276 (March 1950).

Measurements of the magnetic susceptibility and anisotropy have been made on polyethylene terephthalate in various stages of orientation and under various conditions of heat-treatment, and also on dimethyl terephthalate as the nearest analogue to the repeating unit in the polymer. It is deduced that the plane of the dimethyl terephthalate molecule, whilst tilted with respect to all three crystal axes, is roughly parallel to the {010} plane of the crystal. With the polymer, the relation between magnetic anisotropy and draw ratio suggests that in the early stages of drawing the molecular chains are being straightened out. Above a critical draw ratio van der Waals forces begin to be effective, and the chain segments snap into positions of minimum potential energy. At higher draw ratios the fibres tend to become crystalline. Studies of magnetic anisotropy at different annealing temperatures (shrinkage allowed) show that with fibres of low draw ratio there is a drop in anisotropy at about 65°c. followed by only a slight increase, whereas samples of higher draw ratio increase in orientation with annealing temperature. This is thought to be due to the relative freedom of the chains to rotate, the groups in samples of higher draw ratio tending to pull into positions of still better alignment rather than to curl up. P. C.

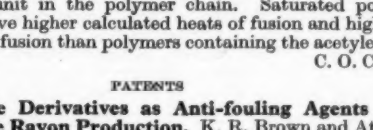
Effect of an Acetylenic Unit on the Physical Properties of Polyesters and Polyurethans. C. S. Marvel and J. H. Johnson. *J. Amer. Chem. Soc.*, **72**, 1674–1677 (April 1950).

Observations made with the polysebacates of butane-1:4-diol and of 2-butyne-1:4-diol and also with the polyurethans of these two glycols with hexamethylene di*iso*cyanate show that the saturated esters and urethans have higher capillary melting points but lower second-order transition points than polymers with the recurring acetylenic unit in the polymer chain. Saturated polyurethans have higher calculated heats of fusion and higher entropies of fusion than polymers containing the acetylenic structure. C. O. C.

PATENTS

Morpholine Derivatives as Anti-fouling Agents in Viscose Rayon Production. K. R. Brown and Atlas Powder Co. *U.S.P.* 2,495,833.

Addition of 0·001–0·1% by weight of a compound of formula—



(R = the same or different C_{1-14} Alk, the total number of C atoms in the three groups being 8–26; X = O, S, SO, or SO_2) to the viscose solution and/or regenerating bath prevents clogging of the spinnerets. C. O. C.

Giving Viscose Rayon more Uniform Dyeing Properties. Algemeene Kunstzijde Unie N.V. *B.P.* 637,106.

Cakes of viscose rayon are arranged with their hollow centres in communication with one another, and then air at 60–90°C. and fully saturated with water vapour is passed through them from the inside to the outside of each cake for not < 15 min. under a pressure of 40–60 cm. of water. This decreases the differences in dyeing affinity. C. O. C.

Continuous Production of Synthetic Twisted or Untwisted Fibres and Yarns suitable for Direct Use. B. Borzykowski and Swiss "Borvisk" Co. *U.S.P.* 2,494,468.

Insolubilising Artificial Filamentary Tows. R. Campbell, W. E. Tetlow, R. H. K. Thomson, and I.C.I. Ltd. *B.P.* 637,025.

Continuously travelling tows of artificial filaments, obtained by spinning aqueous alkaline solutions of vegetable seed globulins or of phosphoproteins into acid saline coagulating baths, are insolubilised by passing them through a helical tubular passage by means of a turbulent stream of aqueous formaldehyde saturated with sodium chloride and containing sodium or magnesium sulphate, at pH 4–6, and then passing them through a second tubular passage by means of another formaldehyde soln. (at a higher temp.), which has been made strongly acid with sulphuric acid and saturated with sodium or magnesium sulphate. J. W. B.

Vinylidene Interpolymers. B. F. Goodrich Co. *B.P.* 636,207.

Products which have high heat stability without addition of stabilisers are made by polymerising a mixture comprising > 30% vinylidene halide, > 1% of a diester of maleic acid, e.g. diethyl maleate, and > 1% of a vinyl ester, e.g. vinyl chloride. W. G. C.

Linear Polyamides. S. J. Allen and J. G. N. Drewitt. *B.P.* 636,348.

Fibre-forming polyamides are obtained by treating a diester of oxalic acid with equimol. proportions of a diprimary diamine without the application of heat, e.g. ethyl oxalate and hexamethylenediamine. W. G. C.

Polyamides containing SO_2 groups. Bata Národní Podnik. *B.P.* 636,198.

Polyamides which can be spun into threads, etc. are made by condensing dicarboxylic acids of formula $(HOOC{\cdot}[CH_2]_m{\cdot}NH)_2SO_2$ (m = 1–15), e.g. the product obtained by treating sulphuryl chloride with the nitrile of 6-aminocaproic acid and then hydrolysing, with aliphatic diamines of formula $H_2N{\cdot}[CH_2]_n{\cdot}NH_2$ (n = 4–15), e.g. hexamethylenediamine. W. G. C.

Phosphite Esters as Stabilisers for Linear Polyamides. D. A. Rothrock, R. F. Conyne, and Röhm & Haas Co. *U.S.P.* 2,493,597.

Linear polyamides are stabilised to moisture, heat, light, and oxygen by heating them at 100–300°C. with 0·001–0·07 mole per kg. of polyamide of a monomeric ester of phosphorous acid whose organic radicals are univalent and free from non-benzenoid unsaturation. C. O. C.

Stretching Polyacrylonitrile Fibres. E. B. Johnson and J. Downing. *B.P.* 636,476.

When yarn containing several continuous filaments of polyacrylonitrile is stretched, the filaments tend to stick together. This can be avoided by stretching the softened yarn while in contact with an aqueous oil emulsion. C. O. C.

Fibre-forming Polyesters. Courtaulds Ltd., E. R. Wallsgrove, and F. Reeder. *B.P.* 636,429.

Polymeric esters which can be cold-drawn to form fibres are made by treating an $\omega\omega'$-dicarboxylic acid or terephthalic acid or an ester derivative with a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups if on the same benzene nucleus are in *m*- or *p*-position and if on different benzene nuclei are in the *p*- and *p'*- or *m*- and *m'*-positions, e.g. succinic acid and quinol diacetate. W. G. C.

Low-methoxyl Multivalent Metal Pectinate Fibres. H. S. Owens, H. Lotzkar, and U.S. Secretary of Agriculture. *U.S.P.* 2,495,757.

Fibres are formed by extruding an aqueous solution of pectinic acids into a precipitating liquor containing multivalent metal ions, e.g. N-$ZnCl_2$ in 95% ethanol. C. O. C.

Silica Fibres. H. I. Thompson Co., L. Parker, and A. Cole. *B.P.* 636,893.

Batts of silica filaments are produced by leaching a resin-bonded batt of glass filaments with e.g. 0·1–5 N-HCl for 20 min. at 60°C., to remove the glass-forming metal oxides but only a negligible amount of silica or resin bonding. If desired the filaments are dehydrated and the resin is removed by firing. J. W. B.

Pile Fabrics. C. F. Taubert and E. H. Taubert. *U.S.P.* 2,495,666.

Pile fabrics are made by compressing wool yarn in a soluble covering, inserting it into a rubber base, and then dissolving the covering on the yarn. C. O. C.

Polymeric Polyamines— Textile Auxiliary Agents, etc., Fibres, Dye Intermediates. H. H. Hoehn and Du Pont. (III, p. 447.)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Studies of Foams. I— Foaminess and Foam Stability of Liquid Mixtures. M. Nakagaki. *Bull. Chem. Soc. Japan*, **21**, 30–36 (Dec. 1948).

The height of the foam zone and the duration and foam stability of the ternary system ethyl alcohol–glycerol–water have been measured. Two maximum points were found, denoting the decrease of surface tension in the region of low concentration of ethyl alcohol, and volume contraction in the region of ~ 45% ethyl alcohol. A third maximum was present in the bubble stability diagram, but absent in the foaminess and foam duration diagrams, and is ascribed to the high viscosity of the system, since it is in the region of high glycerol concentration. The same effect is found also in the case of an aqueous solution of sulphuric acid. H. H. H.

Effectiveness of Detergents in removing Soil from a Cotton and a Wool Fabric. M. S. Furry and V. I. McLendon. *Amer. Dyestuff Rep.*, **39**, 209–212 (3rd April 1950).

The efficiency of a large number of commercial detergents has been determined with both distilled and hard water. The method used was the removal of soil from cotton and wool fabrics as measured by a photoelectric reflectometer. Soaps, anionic agents, cationic agents, and non-ionic agents were tested, and the numerous results tabulated and discussed. W. J. M.

Mechanical Action in the Washing of Fabrics. S. A. Plaksin. *Tekstil. Prom.*, **10**, 29–31 (Feb. 1950).

In order to determine the part played by mechanical action when washing on an open soaper, fabrics were

impregnated in dil. caustic soda, dil. sulphuric acid, starch thickening, or a suspension of Sulphur Black, and then, after drying in the case of the starch and dye impregnations, passed under various conditions through an open soaper containing water only. The amount of material removed was determined. The soaper consisted of four becks, each containing a submerged three-bowl mangle provided with a spurt pipe in front of the second nip. In the first beck the fabric passed over a smooth surface provided with four narrow transverse slits at which powerful suction could be applied. The second beck contained a powerful paddle stirrer on a transverse axis. The third contained an arrangement for forcing liquid through the fabric from narrow slits into wider slits pressed against the opposite side of the fabric. All these mechanical arrangements were submerged. The experiments indicated that the effect of mechanical treatment during washing is very great. The use of the suction or spurt slits increased the rate of removal of the various materials 2–3 times. The use of the spurt pipes increased the rate of removal of electrolyte 15–20%. Starch was removed in appreciable quantity only above 60°C., and it was found that, in this case, the use of the submerged nips was particularly effective. The stirring arrangement increased the rate of removal of starch and pigment by only 20%, but nearly doubled the rate of removal of electrolytes. A. E. S.

Automatic Control of Sodium Hypochlorite Concentration. L. I. Belenky, M. E. Kazanskaya, and N. V. Kasyanenko. *Tekstil. Prom.*, **10**, 26–29 (Feb. 1950).

The electrical conductivity of the working sodium hypochlorite baths used in the continuous processing of fabrics is to be mainly attributed to the sodium hypochlorite itself, the contribution of the other substances present, e.g. sodium chloride, carbonate, and hydroxide, being relatively small. In fact, continuous observations indicated that when the concn. of the bath was controlled manually, there was a close correlation between conductivity and active chlorine content; they also revealed that in normal practice the concn. varied within wide limits. By introducing a feed which was controlled conductometrically, it was found possible e.g. to maintain a concn. of 1·5 g. of active chlorine per litre to within 0·1 g. per litre. The apparatus employed was a modification of standard equipment used for controlling acid and alkali baths. The electrodes were of graphite. The method cannot be used for calcium hypochlorite solutions, as a film of calcium compounds is formed on the electrode system. Methods of control involving automatic titration have not been found satisfactory for technical hypochlorite baths. A. E. S.

Elimination of Boiling in Cotton Bleaching. R. Radu and L. Mayer. *Rev. Teh. AGIR, Textile*, **3**, 62–64 (1949): *Chem. Abs.*, **44**, 1713 (25th Feb. 1950).

The following procedure results in less loss in strength and weight; economy in time, materials, and steam; use of only half the H_2SO_4 usually required; better dyeing properties; and no evolution of Cl_2 gas— (1) Desize with either 1% 66° Bé. H_2SO_4 or 0·2% Na_2CO_3 soln.; (2) circulate water at 50°c. through the materials for 4 hr. in presence of a softener; (3) treat for 2 hr. in aqueous Na_2CO_3 containing NaOCl (2% active Cl); (4) rinse and treat with NaOCl at pH 6·5 for 2 hr. in presence of $NaHSO_3$ (1 g./litre); and (5) treat for 15 min. with 0·5° Bé. H_2SO_4. C. O. C.

Effect of Aniline on Cotton Fabrics bleached with Chlorine. H. Stuhl. *Melliand Textilber.*, **31**, 118–119 (Feb. 1950).

Grey, desized, and kier-boiled cotton fabrics and viscose rayon staple-fibre fabrics given comparable treatments were bleached with chlorine and then given an antichlor treatment in sodium thiosulphate, sodium bisulphite, and hydrogen peroxide. After exposure to aniline vapour all the staple-fibre patterns and all the cotton patterns except those treated with hydrogen peroxide showed pink staining. Chloramine was not detected in the stained patterns, but a blank test on a staple-fibre fabric treated with *p*-toluenesulphonylchloramine and exposed to aniline vapour gave the characteristic stain. Daylight and quartz lamp radiation destroy rather than promote fuchsine formation. Pink staining can be permanently removed by treatment of the goods with hot potassium carbonate solution (1 g./litre). H. K.

PATENTS

Bleaching Natural Cellulosic Fibres. Solvay & Cie. *B.P.* 637,244.

Flax, hemp, jute, etc. are bleached by first boiling them at pH 10·5–12·0 in presence of a Ca- and Mg-sequestering agent and then treating them with active chlorine in an acid medium. C. O. C.

Bleaching Pulp. F. Casciani, G. K. Storin, and Niagara Alkali Co. *U.S.P.* 2,494,542.

A better and more permanent bleach is obtained by— (1) Removal of the non-cellulosic impurities without material loss in strength of the cellulose, e.g. treatment with chlorine, oxidising agents, alkaline extraction, etc. (2) Bleaching with chlorine dioxide in any form, e.g. as gas or weak acid hypochlorite solution. (3) Treatment with a peroxide or organic peracids or their salts. C. O. C.

Peroxide Bleaching. Wolsey Ltd., P. Alexander, and C. Earland. *B.P.* 637,140.

Better-quality goods are obtained if they are treated in a dilute solution of hydrogen peroxide in an inert solvent, e.g. a 2% solution in butyl alcohol, just long enough to wet them thoroughly, after which they are removed from the solution, excess solvent is removed, and the remaining solvent evaporated off the goods.

B.P. 637,150.

Instead of evaporating off the excess solvent, the impregnated goods are heated at 70–100°c., so as to effect bleaching without substantial evaporation of water. Finally the goods are rinsed with water to remove excess hydrogen peroxide. C. O. C.

Bleaching Wool, Skins, Silk, and other Proteinaceous Material of Animal Origin. Solvay & Cie. *B.P.* 636,479.

The material is treated with an aqueous solution of an alkali-metal or alkaline-earth chlorite at pH 4–5. A permanent bleach is obtained without any modification of the other properties of the material. C. O. C.

VIII— DYEING

Dyeing and Finishing of Dress Coatings. Anon. *Wool Record*, **77**, 1207, 1209, 1211 (20th April 1950).

A practical article dealing mainly with the details of crabbing, steaming, scouring, and milling. In dyeing the main requirements are that the dye vessel should be of ample size, that there is no overcrowding, and that the pieces shall be well drafted out. C. O. C.

Importance of the Donnan Membrane for Corrosion Protection by Polar Protective Layers and for Substantive Dyeing. E. Manegold. *Kolloid-Z.*, **116**, 135–146 (March 1950).

Since the migration of ions through capillary membranes, whether of cations or anions, can be hindered by the set-up of electrical equilibria, this fact is now discussed from the standpoint of protection against corrosion by surface layers and also for an explanation of dyeing with substantive dyes. The latter is treated historically, and also deals with the relationship of particle size and electrolytic content to substantivity. There are 11 diagrams. H. H. H.

Formation of Precipitates in Textile Fibres. R. Haller. *Textil-Rund.*, **5**, 94–98 (March 1950).

The distribution of pigments formed *in situ* in natural and artificial vegetable fibres is discussed, with particular reference to inorganic compounds. H. K.

PATENTS

Pigment–Resin Dyeing of Textiles. J. M. Kuhn, W. A. Bodenschatz, and Sherwin-Williams Co. *U.S.P.* 2,488,544.

Addition of not $< 0{\cdot}1\%$ of a water-soluble alginate to emulsions of lacquer-in-water type used for the pad dyeing of textiles results in level dyeings of good appearance. C. O. C.

Dyeing Cellulose with Anthraquinone Vat Dyes. E. Marney and I.C.I. Ltd. *B.P.* 634,973.

The materials are padded with a neutral or acid suspension of a leuco derivative of an anthraquinone vat dye prepared with the help of a dispersing agent, and then treated with aqueous caustic soda, and the dye is oxidised. Pale-to-medium strength, well penetrated dyeings are produced, which have at least the same fastness as similar

dyeings obtained by the usual alkaline reduction process and better fastness to washing than dyeings obtained by the hitherto known methods of applying free leuco compounds of vat dyes. C. O. C.

Dyeing Organic Acid Esters of Cellulose with an Aqueous Solution of a Normally Acid-fading Dye, Lower Aliphatic Alcohol, Thiocyanate, and Alkali-metal Hydroxide. W. H. Hindle and Celanese Corpn. of America. *U.S.P.* 2,495,810.

Greatly improved resistance to acid fading is imparted to acetate rayon dyed by alcoholic solvent dyeing methods if 1–4 g. of an alkali-metal hydroxide per litre is added to the dyebath. Deeper and heavy dyeings are also obtained. C. O. C.

Dyeing Acetate Rayon. British Celanese Ltd. *B.P.* 636,501.

Modification of *B.P.* 583,349 (J.S.D.C., **63**, 196 (1947)). Deeper dyeings with increased fastness to gas fading are obtained by adding a small amount of an alkali-metal hydroxide to the alcoholic dyebath containing an inorganic thiocyanate. C. O. C.

Dyeing Cellulose Esters or Ethers with Indigoid Vat Dyes. British Celanese Ltd. *B.P.* 635,310.

The material is mechanically impregnated with an aqueous suspension of the unreduced indigoid vat dye, then with an aqueous solution of a formaldehyde-sulphoxylate rendered alkaline with an aliphatic hydroxyamine, and then steamed to effect reduction of the dye, and finally the leuco dye is oxidised. This gives full dyeings of very good fastness to rubbing. There is no material saponification of the cellulose ester or ether. C. O. C.

Dyeing Polyvinyl Ester Fibres with Basic Dyes. H. T. Neumann and L. G. Arpin. *U.S.P.* 2,489,537.

Polyvinyl or polyvinylidene chloride fibres or the like dye rapidly when added to a boiling alkaline bath containing a basic dye even while the bath remains colourless. If desired an oxidising agent may be added to speed up the rate of dyeing. C. O. C.

Pattern Effects on Wool Textiles. R. W. Hardacre, S. W. Milne, and I.C.I. Ltd. (IX, this page.)

IX— PRINTING

Chemistry of Chrome Mordants used in Calico Printing. H. Barth. *Melliand Textilber.*, **31**, 120–125 (Feb. 1950).

The history of the application of chrome mordants used in calico printing is briefly described. Examples are given to illustrate the structure of colour lakes and the mode of action of the mordants. H. K.

Fixation of Vat Colours— Some Incidental Ageing Problems. Anon. *Text. Weekly*, **45**, 613, 614, 616, 618, 620 (10th March 1950).

A detailed review is given of the faults which may arise during the ageing of fabrics printed with vat dyes. Thus shade variation may arise from overheating prior to or during ageing, from underdrying after printing, from running too many pieces simultaneously, and from variations in water level where a water bottom is used. The substantial exclusion of air is essential, and in this connection the use of steam-heated draw rollers, ventilators, and other devices is discussed. Faults due to the deposition of print paste on parts of the ager and the subsequent lifting of the deposit by the fabric are discussed at length. This fault, occuring at intake rollers, may be due to a rough roller surface, or to inefficient heating of the roller. The use of a lint doctor is mentioned in this connection. A. E. S.

PATENTS

Pattern Effects on Wool Textiles. R. W. Hardacre, S. W. Milne, and I.C.I. Ltd. *B.P.* 635,114.

Wool textiles are printed with an acid or acidic substance, then treated with an aqueous hypochlorite, and finally dyed to produce contrasting or tone-in-tone effects depending on the dyes used. C. O. C.

Yarn-patterned Fabrics. Sayles Finishing Plants Inc. *B.P.* 635,157.

Nylon yarns are woven into a suitable pattern with cellulosic or protein yarns and then treated chemically to remove certain portions of one of the yarns, preferably the cellulosic or protein, while leaving at least one of the other yarns unaltered. Thus cellulosic yarns are removed by printing with aluminium sulphate or chloride and heating at 250°F. for 10–20 min., and protein yarns by printing with caustic soda and then steaming slightly above atmospheric pressure for a few minutes. Alternatively, the fabric may be printed with a resist and then carbonised to remove unresisted cellulose yarns. C. O. C.

Screen Printing. F. Jane. *B.P.* 634,710.

The material to be printed is stretched on the printing table by guide rollers, one of which acts as a feed roller. The screens are placed at equal distances from a vertical axis on a frame which can rotate or oscillate about that axis. This frame can be raised or lowered with the screens, so that they can rest successively on the material on the table. By arranging a number of tables around the axis of rotation of the frame, simultaneous printing of a number of pieces of material is possible. C. O. C.

Diazotype Aqueous Coating Solutions for Regenerated Cellulose and Cellulose Esters and Ethers. C. Botkin and General Aniline & Film Corpn. *U.S.P.* 2,496,196.

Coatings containing a light-sensitive diazo compound and ethylene or propylene chlorohydrin can be applied without formation of scum. C. O. C.

Sulphoaminobenzoic Acids and their *N*-Substituted Derivatives as Stabilisers for Diazotype Compositions. W. H. von Glahn, L. N. Stanley, and General Aniline & Film Corpn. *U.S.P.* 2,496,240.

Setting Printing Inks with Sulphur Dichloride. Meyercord Co. (V, p. 454.)

X— SIZING AND FINISHING

Soluble Starch Size. V. M. Rybakova. *Tekstil. Prom.*, **10**, 27–28 (Jan. 1950).

A weaver's size, which has very satisfactory stability, adhesion, and viscosity, may be prepared by the action of chloramine T on starch. The breakdown of starch by chloramine does not readily proceed beyond a certain stage, and the conditions of preparation may be varied within wide limits without altering the properties of the final product to an appreciable extent. This is illustrated by experiments in which the concn. of chloramine, the time and temperature of reaction, and the pH of the medium were varied. A size was prepared by adding chloramine (0·5% on the wt. of starch) to a 7·5% suspension of potato starch and heating at 90°C. for 100 min. When the proportion of chloramine was increased to 2·5% and the duration of heating to 4 hr., the properties of the resulting size were substantially unchanged. The addition of acid or alkali (pH 2·9–10·7) increased the rate of breakdown, but did not affect the nature of the resulting product to an appreciable extent. Measurements were made of the extensibility and tensile and abrasion properties of cotton yarns sized with chloramine-solubilised starch. Some account is given of results obtained in U.S.S.R. weaving practice, where the use of this size is now extending rapidly. A. E. S.

The Weavers and Fullers of Marlborough. K. G. Ponting. *Wiltshire Archæological & Natural History Magazine*, **53**, 113–117 (June 1949).

Historical, mainly concerned with the 12th and 13th centuries. C. O. C.

Production of Melamine–Formaldehyde Resins on Cotton Fabrics. F. I. Sadov and E. O. Vildt. *Tekstil. Prom.*, **10**, 29–31 (Jan. 1950).

A disadvantage of melamine–formaldehyde treatments for fabrics is the necessity for special curing apparatus. High-temp. curing may, however, be replaced by a simple treatment on ordinary drying cans if the precondensate is prepared as follows— Commercial formalin (not $< 35\%$ CH_2O) is neutralised to pH 7·5–8 with *N*-NaOH, and heated to 77°C. The mixture is stirred constantly and melamine is sprinkled in, the molar ratio of melamine to formaldehyde being 1 : 3. The temp. rises to 80°C., and is maintained at this value for 1 hr. The mixture is then cooled and diluted to the required concn., formic acid (1 mole per mole of melamine) being added as catalyst. Other catalysts were examined— ammonium salts require a high curing temp., and acetic acid does not promote a good

yield of insoluble resin. Fabrics treated in the recommended way have good crease-resistance, low water uptake, and high dimensional stability. The tendering of white and dyed fabrics on exposure to light is considerably reduced by the application of the resin finish.
A. E. S.

Rotproofing. H. W. Partridge and G. E. Key. *J. Textile Inst.*, **40**, P 1077–P 1089 (Dec. 1949).

Rotproofing and the use of a number of rotproofing agents are discussed, and a method of precipitating copper naphthenate inside the fibre is described. Ammonium naphthenate mixed with cuprammonium solution of equivalent strength gives an apparently stable solution, in which the fabric is immersed. On drying, the ammonia volatilises and the insoluble copper naphthenate is formed. This method is superior to the use of solvents or colloidal dispersions, and it can be modified for zinc naphthenate where the colour of the copper compound is a disadvantage. The use of quaternary ammonium salts in conjunction with phenolic compounds gives an insoluble compound which is extremely effective. The results of soil burial and incubation tests illustrate the relative efficacies of various treatments. The use of Shirlan followed by cetylpyridinium bromide is incomparably better than Shirlan alone, and in fact than any of the other treatments tried. W. J. M.

Microbiological Degradation of Cellulose. G. A. Greathouse. *Text. Research J.*, **20**, 227–238 (April 1950).

Recent studies on the mechanism of the microbiological degradation of cellulose are reviewed and some new data presented. Cellulose derivatives substituted at various positions in the molecule were exposed to the action of *Myrothecium verrucaria*. Cellulose acetate ($> 9{\cdot}3\%$ acetyl), cellulose triacetate, ethyl cellulose (45·8% ethoxy), methyl cellulose, and 6-cyanoethyl cellulose were completely resistant, as were also cellobiose octa-acetate and penta-acetyl glucose, suggesting that chemical blocking of the alcoholic groups prevents attack by this fungus. Some data on the isolation and properties of an enzyme preparation from *M. verrucaria* are given, and it is suggested that further work on this subject is needed. There are 65 references to the literature. P. C.

Impact of Raindrops on Fabrics. M. Karrholm and G. Karrholm. *Text. Research J.*, **20**, 215–226 (April 1950).

Using a high-speed motion-picture camera a study has been made of the pressure–time relationships existing during the impact of raindrops on a solid foundation, e.g. fabric. A mathematical treatment of water-drop impact is given. Experiments with thin acetate film and a water-repellent cotton fabric showed that the upper part of the drop retained its spherical shape and had the same velocity as at the beginning of impact, while in the lower part of the drop the water was pressed outwards as a continuous film. The upper limit of pressure developed between the drop and the foundation it strikes is given by two equations, one of which is dependent on the modulus of elasticity of the surface of the foundation. It is shown that plain fabrics will be affected by much higher pressures in rain than napped fabrics, and therefore for the former to be rain-resistant the pores must be small. Certain conclusions concerning the testing of water-repellent fabrics are given. P. C.

Impregnation of Fabrics with Aqueous Dispersions of Hydrophobic Substances. S. S. Voyutsky and Ya. M. Yabko. *Tekstil. Prom.*, **10**, 22–25 (Feb. 1950).

In the first of a series of articles on the production of water-repellent finishes, the wetting properties of various organic liquids and aqueous solutions of emulsifying agents on cotton material are examined and correlated with surface tension and contact angle measurements. The surface tension γ_{GL} of the liquid against air shows a poor degree of correlation with wetting, and of the thermodynamic properties examined, the work of wetting $\gamma_{GL}(\cos\theta - 1)$, where θ is the angle of contact, is found to give the closest correlation with the measured wetting effect. Angles of contact are measured against cellulose nitrate film, and these values are considered to be close to those obtaining at the surface of cotton fibres. It is found that emulsifying agents of the surface-active type and those of the protective-colloid type may be mutually antagonistic in mixtures, no doubt due to the adsorption of the former on the colloidal particles of the latter.
A. E. S.

Effect of Non-durable Aluminium Salt–Wax Emulsions on the Wear Resistance of Textiles. S. J. Tanenhaus and M. E. Darby. *Amer. Dyestuff Rep.*, **39**, 349–356 (29th May 1950).

Claims that the use of non-durable aluminium salt–wax emulsions decrease the amount of soiling and increase the serviceability of textile materials are evaluated by three field service trials, the conditions being respectively (*a*) severe wear and moderately severe laundering, (*b*) moderate wear and very severe laundering, and (*c*) moderate wear and laundering. It is concluded that the use of these non-durable products is justified only in case (*c*). Moreover, field serviceability cannot be predicted by standard laboratory tests, including yarn and fabric strength, extractable matter, and cuprammonium fluidity tests, which were also carried out. J. W. B.

PATENTS

Wet-processing of Yarns. British Celanese Ltd. *B.P.* 636,926.

Yarns are treated with fluid under pressure during their passage from one point to another, by leading them into a closed chamber having a yarn outlet and a common yarn-fluid inlet, the latter being a diverging tube into which the yarn is led without prior contact with the fluid. By incorporating a stretching device, thermoplastic yarns, e.g. cellulose organic esters, may be stretched beyond their elastic limit while in suitable media, e.g. wet steam.
J. W. B.

Parallel-fibre Material. J. E. Gordon and C. G. Evans. *B.P.* 636,237.

Material containing substantially parallel fibres is prepared by impregnating a fibrous yarn, the twist of which maintains the fibres parallel, with liquid adhesive, and untwisting, when the parallel relationship is maintained by the adhesive. Using a partly condensed synthetic resin a multiplicity of yarns may be so treated, untwisted, laid together, and formed by curing into a laminated reinforced sheet. J. W. B.

Yarns and Fabrics containing Continuous Filaments but resembling those wholly of Staple Fibres. United Merchants & Manufacturers Inc. *B.P.* 636,688.

A composite yarn is formed having a continuous-filament nylon core and a wrapping of staple fibres. The yarn or fabric containing such yarn is treated with either boiling water or high-pressure steam so as to cause interlocking but not permanent adhesion between the core and the wrapping. Such yarns or fabric have the subdued lustre and handle of spun yarns or fabrics wholly made from them, but are stronger, dimensionally more stable, and more serviceable than the latter yarns or fabrics.
C. O. C.

Setting Thermoplastic Fabrics. J. E. Roberts and R. C. Parkes. *U.S.P.* 2,488,937.

The fabric is passed over a substantial portion of the surface of a rotatable hollow roll containing a liquid. Means are provided for heating the liquid, which is caused to flow longitudinally in the roll when the roll is rotated, being directed by a vane extending longitudinally inside the roll and forming an angle with its axis, so that the liquid flows in one direction in one part of the roll to one side of the vane and in the opposite direction in another part of the roll to the other side of the vane. This enables the surface temperature of the roll to be both satisfactorily controlled and kept uniform. C. O. C.

Imparting Crease- and Fire-resistance to Cellulosic and Protein Fibres. Courtaulds Ltd., T. H. Morton, and F. Ward. *B.P.* 634,690.

The materials are impregnated with an aqueous solution containing a strong non-volatile mineral acid and cyanamide, and are then baked at a high temperature to produce a reaction product of cellulose (or protein), acid, and cyanamide. The strength of the solution and conditions of processing should be such that after baking the fibres contain not $< 1\%$ by weight of combined acid and preferably not $< 3\%$ of their weight of combined acid and cyanamide. C. O. C.

Crease-resistant Finish. L. Balassa and United States Finishing Co. *U.S.P.* 2,493,381.

The fabric is impregnated with an aqueous solution of

a thermosetting polymerisable resin. A discontinuous layer of solid, water-insoluble, finely divided, hydrophilic material is then applied to the impregnated textile before it is dried, or the hydrophilic material is intimately mixed with the excess solution on the fabric surface, e.g. by brushing china clay on to the moist material. The mixture of hydrophilic material and excess resin solution is then removed, thus clearing the fabric of any excess free resin solution, after which the resin is insolubilised in presence of an acid catalyst. The catalyst may be applied at the same time as the hydrophilic material. The finished fabric has no surface resin on the fibres, and so has impro ved handle, tensile strength, and abrasion resistance. C. O. C.

Durable, Lustrous, Colourless or Dyed Pattern Effects. W. P. Hall and Joseph Bancroft & Sons Co. *U.S.P.* 2,488,397.

The fabric is impregnated with an aqueous size and/or an organic base capable of coupling with a diazo compound to give a dye. The fabric is dried after being sized. It is then printed with an aqueous printing solution containing a water-soluble thermosetting resin which becomes insoluble in water when polymerised, a printing gum, a textile lubricant, and, in the case of the base-impregnated fabric, a suitable diazo compound. The printed fabric is dried to dampness and friction-calendered, and the resin cured, the cure being partly or wholly effected during the calendering. The aqueous size used should contain 3–13% of a printing gum compatible with the printing paste and 1–2% of a textile lubricant, the proportion used being such as to impart the same frictional characteristic to the unprinted areas as to the printed areas of the fabric. C. O. C.

Lustrous Finishes. Joseph Bancroft & Sons Co. *B.P.* 635,923.

The fabric is impregnated with an aqueous solution of thermosetting resin-forming material containing a non-waxy sulphonated oil having a chain of > 8 C, dried, passed through a hot glazing calender, and then washed to remove the oil and unreacted material. The amount of the oil used is such as to prevent the resin from sticking to the calender rolls. C. O. C.

Dimensional Stabilisation of Cellulosic Textiles. R. J. Smith, C. D. Weston, and I.C.I. Ltd. *B.P.* 635,034.

The materials are impregnated with a solution or dispersion of pyruvic aldehyde in presence of an organic acid and then heated at 120–160°c. for 5 min. C. O. C.

Non-slip Fabrics containing Synthetic Fibres. A. D. Nute and American Cyanamid Co. *U.S.P.* 2,491,454.

Fabrics containing nylon, etc. threads are impregnated from aqueous solution with about 3–20% of their weight of a water-soluble alkylated methylolmelamine and then heat-cured. C. O. C.

Mechanical Finishes fast to Washing and Dry Cleaning. Joseph Bancroft & Sons Co. *B.P.* 634,634.

Durable lustrous mechanical effects on fabric of cellulose and regenerated cellulose fibres are obtained by sizing the fabric with a polysaccharide carbohydrate and formaldehyde, paraformaldehyde, glyoxal, acetaldol, hexamethylenetetramine, or polymerisation products of formaldehyde. The carbohydrate and the aldehyde are applied in aqueous solution either separately or together either in unreacted or partly reacted state, in either case the weight of aldehyde being 0·5–5% of the weight of the solution in which it is applied. After sizing the fabric is dried to dampness, given a lustrous mechanical finish, and finally cured at 280–400°F. C. O. C.

Raising the Safe Ironing Point of Acetate Rayon. C. Dreyfus, G. W. Seymour, G. C. Ward, and Celanese Corpn. of America. *U.S.P.* 2,488,587.

The materials are impregnated with 1–15% aqueous boric acid, dried, and then heated to not < 110°c. under not < 2000 lb./sq. in. pressure. In addition to raising the safe ironing point, the ironing properties, e.g. handle, draping qualities, etc., are also improved. C. O. C.

Raising the Safe Ironing Temperature of Non-thermoplastic Fibres. C. Dreyfus, G. W. Seymour, G. C. Ward, and Celanese Corpn. of America. *U.S.P.* 2,488,588.

The resistance of non-thermoplastic fibres to scorching at higher ironing temperatures is increased by treating them with 1–15% aqueous boric acid and then heating at 110–150°c. and a pressure of 2000–8000 lb./sq. in. C. O. C.

Shrinkproofing Wool. J. B. Rust and Montclair Research Corpn. *U.S.P.* 2,491,584.

Interpolymers of compounds of formula $CH_2{:}CR^1{\cdot}CR^2{:}CH_2$ (R^1 = H or lower alkyl; R^2 = H, lower alkyl, or Hal), e.g. 1:3-butadiene, with unsaturated ketones of formula $CH_2{:}CR^3{\cdot}CO{\cdot}R^4$ (R^3 = H, Alk, or Ar; R^4 = Alk or Ar), e.g. *iso*propenyl methyl ketone, are used to render goods containing wool or other protein fibres shrink-resistant. The goods to be treated are impregnated with an aqueous emulsion of the interpolymer, which has been preferably 100% polymerised so as to obtain cross-linking. The interpolymers may be vulcanised either before or after application to the material or its dyeing. C. O. C.

Acid-resistant Textile Fibres. J. D. Reid, W. K. Ward, L. W. Mazzeno, and U.S. Secretary of Agriculture. *U.S.P.* 2,493,031.

Textile fibres are rendered resistant to acid vapours by impregnating them with alkaline, buffering, humectant agents; e.g. cotton sewing thread for paper bags for acidic fertiliser is impregnated with at least 20% by weight of triethanolamine. C. O. C.

Organopolysiloxane Coating Compositions. E. L. Warrick and Corning Glass Works. *U.S.P.* 2,494,920.

A highly tenacious water-impervious and water-repellent coating is obtained on textiles, siliceous materials, etc. by applying a thin film of an organosiloxane, heating to 180–400°c. in not > 2 min., and keeping the temperature constant until the coating is cured. C. O. C.

Dyeing and Finishing of Dress Coatings. Anon. (VIII, p. 456.)

Pattern Effects on Wool Textiles. R. W. Hardacre, S. W. Milne, and I.C.I. Ltd. (IX, p. 457.)

Yarn-patterned Fabrics. Sayles Finishing Plants Inc. (IX, p. 457.)

Identification of Crease-resist Finishes. H. M. Ulrich. (XIV, p. 464.)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Green Colour produced by Acids on Wood and the Lignin–Cellulose Complex. F. A. Abadie. *Norsk Skogindustri*, **3**, 290–294 (1949): *Chem. Abs.*, **44**, 3249 (10th April 1950).

The green colour appearing when wood flour is treated with strong mineral acids is due to a lignin–carbohydrate complex, this colour also being given by the lignin–carbohydrate complex which is the acetone-insoluble fraction of nitrated semi-chemical pulp. This colour reaction should have practical significance as a simple test for approximate estimation of the extent to which carbohydrates are bound to lignin in semi-chemical pulps. C. O. C.

PATENTS

Coated Fibres of Cellulosic Material and Felted Fibrous Cellulosic Material embodying them. American Cyanamid Co. *B.P.* 637,227.

A water-insoluble coating agent containing essentially a wax, a bitumen, a gum, a resin, an elastomer, or a thermoplastic or thermosetting synthetic resin, e.g. polystyrene, is applied to cellulosic fibres by suspending them in water, adding an aqueous dispersion of the deflocculated coating agent, and flocculating it in the presence of the fibres by the action of a colloidal dispersion of cationic melamine–aldehyde resin in sufficient quantity to provide at least 5% by weight of coating agent, based on the weight of fibres, for uniform dispersion thereon along with the resin. If desired, the resin dispersion (2–30%, preferably 2–15% of the weight of coating agent) may be added, and the fibre suspension (0·5–6% consistency) may stand in non-alkaline condition, e.g. pH 3–6, for at least 30 min. before the coating agent is introduced. The coating agent may contain an anionic or non-ionic emulsifier, and be added up to 50–100%, based on the dry weight of the fibres. Felted fibrous cellulosic material is made from the coated fibres, the water draining from them depositing the flocculated but unabsorbed coating agent in the felted product. S. V. S.

Paper Pulp Composition useful for Coating Surfaces or making into Sheets. K. Malling. *B.P.* 636,665.

A composition useful as a priming coat for paints or varnishes or as a base for linoleum consists of not < 50% paper pulp, not < 30% kieselguhr free from clay, and < 20% (based on the other two components) of a binder or adhesive. C. O. C.

Alkali Cellulose Derivatives. M. H. Wilcox, J. Downing, and J. G. N. Drewitt. *B.P.* 637,133.

Alkali cellulose is made by mixing cellulose of packing density > 10 lb./cu. ft., without grinding, with solid caustic alkali in presence of an ether-alcohol, e.g. 20% by wt. of monomethyl glycol. The product may be treated with an etherifying agent, e.g. ethyl chloride, to give cellulose ethers.

B.P. 637,134.

Cellulose ethers are made by subjecting cellulose to the action of an etherifying agent, e.g. methyl chloride, ethyl chloride, or chloroacetic acid, in presence of an aqueous caustic alkali and 10–30% (on wt. of cellulose) of a liquid ether-alcohol, e.g. a partial lower alkyl ether of a glycol or glycerol, e.g. monomethyl glycol. J. W. B.

Insolubilisation of Cellulose Ethers and Esters. E. K. Morris and Dow Chemical Co. *U.S.P.* 2,489,225.

Any thermoplastic cellulose ether or ester containing residual OH groups can be rendered insoluble in organic solvents by treating it first with 10% of its weight of phosphorus trichloride at not > 40°c., and then with a primary or secondary aliphatic amine of 1–3 C, removing the water-soluble reaction products, and drying. C. O. C.

Cellulose Organic Esters. J. F. Neilson and J. A. Hawkes. *B.P.* 637,267.

Cellulose esters are prepared by esterifying cellulose with an anhydride of a lower aliphatic acid, e.g. acetic anhydride, in presence of a solvent for the ester formed, with 0·8–10% of sulphuric acid and 0·2–2% of perchloric acid, on the wt. of cellulose, as catalyst. J. W. B.

Cellulose Propionate. British Celanese Ltd. *B.P.* 637,342.

Thermoplastic material with high resistance to blushing is produced by using cellulose propionate which has been fractionally precipitated by alcohol from solution in acetone. J. W. B.

Cellulose Esters of High Clarity. British Celanese Ltd. *B.P.* 637,650.

Plasticising Composition for Cellulose Esters and Ethers. A. J. Geiges and Baker Castor Oil Co. *U.S.P.* 2,495,714.

A viscous, oily diester of pentaerythritol mixed with dehydrated castor oil fatty acids forms a composition which improves the pliability, toughness, resistance to cold, etc. of cellulose esters and ethers. C. O. C.

Chemistry and Application of Sulphonamide Resins. A. Kraus, A. Lendle, and S. A. Polaine. (XIII, this page.)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

PATENT

Waterproofed Leather. C. G. Shaw. *B.P.* 637,095.

Leather is waterproofed without loss of resilience by impregnation with a molten waterproofing substance, e.g. fat, grease, or wax, which is normally brittle and of m.p. not < 50°c., excess being removed by wetting the grain and flesh sides with an aqueous detergent above the wax m.p., which swells the leather fibre and thus expresses the wax, the residue being hardened by quick cooling. J. W. B.

XIII—RUBBER; RESINS; PLASTICS

Chemistry and Application of Sulphonamide Resins. A. Kraus, A. Lendle, and S. A. Polaine. *J. Oil & Col. Chem. Assocn.*, 33, 159–174 (April 1950).

The history and chemistry of the manufacture of sulphonamide resins are reviewed. It is suggested that sulphonamide resins differ from other resins and polymers in that they are supercooled melts in which the resinous nature is not produced by normal valency bonds, but by the action of associative or van der Waals forces. The physical and chemical properties of the unmodified and modified resins are described. Because of their solvent action on cellulose nitrate they are largely used in lacquers. Some of the softer types produce highly supple films, and may therefore be used in paper and textile finishes. C. O. C.

PATENTS

Continuous Coagulation of Latex. B. F. Goodrich Co. and W. F. Bixby. *B.P.* 636,425.

Natural or synthetic rubber latices are continuously converted to rubber sheet in machinery which comprises tanks in which the latex is first stabilised and then coagulated, a disintegrator for regulating crumb size, a continuous wire mesh on which the crumb is washed, and squeeze rolls and a hot air oven in which the crumb is consolidated to sheet and dried. E. C.

Ornamented Rubber Sheeting. Kenworth (Australia) Proprietary Ltd. *B.P.* 637,384.

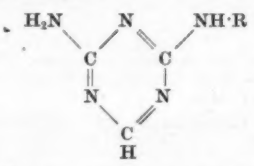
Rubber sheeting is ornamented by shaped pieces of cured or partly cured rubber embedded in its surface, the pieces having been first assembled on a transfer sheet to form the required design, and then applied to the uncured plastic sheet, in which they are permanently bound by subsequent vulcanisation. J. W. B.

Catalyst for Vinyl Chloride Polymerisation. B. F. Goodrich Co. *B.P.* 636,232.

Vinyl halides are polymerised or copolymerised by conventional methods using as catalyst < 5% of an inorganic reducing agent containing S and O, e.g. sulphur dioxide, sodium bisulphite. Other types of catalyst may be employed simultaneously. E. C.

Azoguanamines— Components for Coloured Resins. J. T. Thurston, D. W. Kaiser, and American Cyanamid Co. *U.S.P.* 2,493,703.

Compounds of formula—



(R = an arylene azo-aromatic radical, the bond between the N on the 4-carbon atom of the triazine ring and R being an N–C linkage), e.g. *N*-*p*-(4-hydroxy-3-diphenyl)-azophenyl-formoguanamine, can be condensed with aldehydes to yield coloured resins. C. O. C.

Colourless Polymers of α-Halogenoacrylic Acids and their Derivatives. General Aniline & Film Corpn.

Discoloration of α-halogen-substituted acrylic resins is said to be due to presence of oxalyl halide compounds, e.g. methyl oxalyl chloride in methyl α-chloroacrylate monomers. In this series of patents substances are described which do not introduce colour, but convert the oxalyl halide compound into a non-colour-forming compound, thereby resulting in a monomer capable of forming a colourless polymer. It is not necessary to polymerise the monomer in absence of air or to remove the autoxidation products—

With C. E. Barnes. *B.P.* 636,318.

Addition of > 0·1% of a polymerisable ester of a polyhydric alcohol, differing in structure from the acrylic acid derivative and interpolymerisable with it, e.g. ethylene glycol monoacrylate.

With C. E. Barnes. *B.P.* 636,322.

Addition to the monomer of > 0·1% of an ester of an organic hydroxy acid which is soluble in the monomer as well as in the corresponding polymer, e.g. vinyl glycollate.

With C. E. Barnes and W. O. Ney. *B.P.* 636,319.

Addition to the monomer of 0·1–15% of a monohydric alcohol, e.g. methyl, ethyl, or propyl alcohol.

With C. E. Barnes and W. O. Ney. *B.P.* 636,321.

Addition to the monomer of 0·1–5% of a neutral ester of an alcohol with an inorganic acid, e.g. dipropyl sulphite.

With W. O. Ney. *B.P.* 636,320.

Polymerisation in the presence of water or aqueous alcohol in amount which dissolves completely in the monomer.

With C. E. Barnes and W. O. Ney. *B.P.* 636,323.

Addition of 0·1–6% of a polyhydric alcohol, e.g. glycol, or a partial ester or ether thereof, during preparation of the α-halogenoacrylic acid by dehydrohalogenating the ester of a dihalogenopropionic acid containing at least one halogen atom in the α-position. W. G. C.

Butadiene–Acrylonitrile Copolymers—Leather-like Resins. B. F. Goodrich Co. *B.P.* 636,055.

Tough, leather-like resins of excellent solvent resistance are prepared by conventional emulsion polymerisation of acrylonitrile with less of a compound of formula CH_2:CR·CR:CHR (R = H or CH_3), e.g. butadiene. E. C.

Butadiene–Styrene–Acrylonitrile Copolymers. B. F. Goodrich Co. *B.P.* 636,361.

Copolymers of 65–80% of butadiene with 35–20% of a mixture of approximately equal parts of styrene and acrylonitrile are prepared by conventional methods. They show limited swelling in petrol and are suitable for preparing self-sealing fuel hose. E. C.

Coloured Designs on Thermoplastic Substances. Welch Holdings Ltd. and K. O. Berry. *B.P.* 637,169.

Coloured designs are formed on fully processed thermoplastic materials by placing on the surface a coloured thermoplastic substance in the required design, heating to fuse them together, and if desired pressing to form a level or embossed surface. J. W. B.

Synthetic Adhesive. General Aniline & Film Corpn. and I. V. Runman. (III, p. 447.)

Phosphite Esters as Stabilisers for Linear Polyamides. D. A. Rothrock, R. F. Conyne, and Röhm & Haas Co. (VI, p. 455.)

XIV—ANALYSIS; TESTING; APPARATUS

Method for the Characterisation of Membranes and Diaphragms. J. K. Wirth. *Kolloid-Z.*, **116**, 147–160 (March 1950).

Although capillary systems in general are regulated by a flow mechanism, no method has existed hitherto for the measurement of their pore dimensions which affords results which are reproducible or free from objections on physical grounds. Such a method is now described, with comprehensive theoretical and experimental treatment, whereby accurate data may be obtained. There are 8 diagrams and numerous tables. H. H. H.

Opacity of White Pigments with special reference to Titanium Dioxide. E. G. Rutter. *Paint*, **20**, 161–169 (May 1950).

Work with a photoelectric integrating-sphere photometer has shown that Smith and Amy's equations—

$$\coth kc = 1 + \frac{2R_\infty}{1-R_\infty^2}\left(\frac{1}{R} - \frac{1}{R_\infty}\right)$$

$$\text{and } \frac{1}{T} = \cosh kc + \frac{1+R_\infty^2}{1-R_\infty^2}\sinh kc$$

(k = a constant, c = pigment concentration as weight per unit area, R = measured reflectance, R_∞ = reflectance of an infinitely thick film, T = transmittance) are simultaneously true provided that the found values of reflectance I are corrected for the gloss of the varnish layer lying above and under the pigments. Films were prepared on regenerated cellulose film (n approx. 1·5), so that the film consisted of a sandwich of pigment between layers of clear material. The refractive index n of all common varnishes lies between 1·49 and 1·5. For many measurements the sandwich had several layers, but as the found values agree so well with those calculated it is believed that only the boundary layers are significant. The gloss correction is given by—

$$I = \frac{R + (an^2 - 1)(1-R)}{R + (2an^2 - 1)(1-R)}$$

($a = 1 +$ the diffuse reflection coefficient for a clear sheet of refractive index n calculated from McNichola's partial integration of Fresnel's formula (*Bur. Stand. J. Res.*, **1**, 50 (1928)), or by—

$$I = \frac{(1-x)}{2}\left[\frac{R+T}{1-x(R+T)} + \frac{R-T}{1-x(R-T)}\right]$$

(x = internal diffuse reflection coefficient calculated from the above formula). The application of these measurements to the determination of the commercial value of white pigments is discussed. C. O. C.

Paper Chromatography of Anthraquinone Pigments. S. Shibata, M. Takito, and O. Tanaka. *J. Amer. Chem. Soc.*, **72**, 2789, 2790 (June 1950).

Procedures for separation, identification, and determination of R_f-values of several synthetic and natural hydroxyanthraquinones are described. C. O. C.

Light Fastness of the Madder Lakes of Alizarin and its Congeners. V. V. Kozlov and K. M. Sidneva. *J. Appl. Chem.* (*U.S.S.R.*), **23**, 317–326 (March 1950).

Preparations of the calcium–aluminium lakes of some hydroxyanthraquinones and their derivatives were dispersed in oil, and exposed on a paper base to sunlight and to the light of a quartz mercury lamp. The following order of light fastness was found—purpurin-3-carboxylic acid > purpurin-3-sulphonic acid > purpurin > alizarin > quinizarin > anthragallol > 1:2:3:4-tetrahydroxyanthraquinone. A. E. S.

Polarographic Determination of Phthalimide, Isatin, Dioxindole, and Indigo Carmine. I. A. Korshunov, L. N. Sazanova, M. K. Shchennikova, and O. P. Malkova. *Zavodskaya Lab.*, **15**, 1287–1290 (1949): *Chem. Abs.*, **44**, 3846 (10th May 1950).

Phthalimide is determined in acid solution (buffered at pH 5 or 0·1–1·0N-HCl) with a half-wave potential at 25°c. in 0·2N-HCl of − 0·7 v. Isatin can be determined in acid or alkaline solution with a half-wave potential at pH 2·64 of − 0·28 v. or in 0·1–1·0N-NaOH of − 1·45 v. Dioxindole undergoes transformations at pH > 4 giving varying wave forms with time; at pH 2·64 its half-wave potential is − 0·29 v. Indigo Carmine gives stable waves at pH 1·5–11·0; the half-wave potential varies with concentration: at pH 2·64 it is − 0·24 v. at 0·004 M. concentration and − 0·4 v. at 0·03 M. C. O. C.

Evaluation of Red Lead Pigments. III—Autocatalysis in Paint Sedimentation. IV—Improvement of Dispersion Stability of the Paints. A. Jogarao. *J. Sci. Ind. Research* (India), **8B**, (11), 195–206 (1949): *Chem. Abs.*, **44**, 4691 (25th May 1950).

III—The sedimentation rates of "ordinary", "non-setting", "high-disperse", and "superfine" red leads were examined, in presence and in absence of a dispersing agent; all had a normal sedimentation velocity. The superfine sample, when made into a paint with 0·75% aluminium stearate in a mixture of raw and double-boiled linseed oils and dispersed in white spirit, gave a distinct S-shaped curve; this autocatalytic behaviour tended to disappear gradually as time went on from the formation of the paint. After 24 hr. normal behaviour was noted; after 47 hr. the sedimentation rate again failed to conform to the normal type, indicating complicating factors arising from precipitation of lead soap gels. The importance of specifying a lower particle size limit is stressed. Exposure tests indicated earlier rust appearance on panels painted with superfine red lead than with the comparatively coarse pigments. Thin layers of small pigment particles are more readily affected by light than tinctorially equivalent layers of larger particles. In near-colloidal paint systems the inert diluent is no longer inert, but acts as a coagulator, causing flocculation or aggregation. The quality of pigments cannot be increased indefinitely by increasing the fineness of the particles.

IV—Red lead (10 g.) was worked into a stiff paint with 3 c.c. of a mixture of raw and double-boiled linseed oil (1 : 2 by vol.). This was thinned to 300 c.c. with white spirit in a modified Kelly sedimentation tube. Optimum dispersion stability was obtained by using 0·5–0·75% aluminium stearate (on wt. of pigment) as a dispersing agent. Total replacement of the usual linseed oil mixture by stand oil improved the dispersion stability to the same extent as the optimum amount of aluminium stearate. This was also true of using 5% (on wt. of pigment) of plaster of Paris. C. O. C.

Analysis of Lead Naphthenates. A. Castiglioni. *Ann. Chim. applicata*, **39**, 197, 198 (1949): *Chem. Abs.*, **44**, 4692 (25th May 1950).

The Pb is extracted with ether after treating with acetic acid to convert to lead acetate, and is then determined as chromate. C. O. C.

Determination of Cobalt in Naphthenate Driers. H. B. Gordon and W. D. Lang. *Paint, Oil Chem. Rev.*, 113, (2), 14, 16–18, 42, 43 (1950): *Chem. Abs.*, **44**, 4691 (25th May 1950).

Comparison of electrolytic, gravimetric, and potentiometric methods shows the last to be the best for industrial use and less subject to error caused by common contaminants. C. O. C.

Moisture Determination in Textiles by Electrical Meters—IV. J. C. Whitwell, C. F. Bowen, and R. K. Toner. *Text. Research J.*, **20**, 400–409 (June 1950).

This paper describes the comparison of electrical moisture meters used for sheet materials, e.g. fabrics. Two instruments, viz. the Fielden Drimeter and the Hart Moisture Meter, were tested. The standard deviation of the former, based on the laboratory tests described, is ± 0·14% moisture (cf. 0·12% for the oven method). Calibration is affected by abnormal temperature variation, tension variations, and the presence of certain impurities, e.g. salt, but such variations should not normally occur in mill operation. The Hart instrument has a standard deviation of ± 0·07% moisture. For both instruments the values of the standard deviations depend upon the experimental conditions used in these tests. P. C.

Rapid Analytical Method for Determination of Changes in Cotton and Cotton Fabrics. O. Heim. *Amer. Dyestuff Rep.*, **39**, P 417–P 418 (26th June 1950).

An analytical procedure is described which enables latent damage, incurred during the processing of cotton materials, to be measured much more simply than by the cuprammonium fluidity method. Stock solution is prepared as follows— Water (20 parts by wt.) is mixed with zinc oxide (9), and caustic soda (20) is added until a clear solution results when a few drops are added to 2 ml. of distilled water. The soln. is cooled, and water (31) added. 40 g. of this solution is diluted with 50 g. of water, and 5 g. of dry cotton, desized and with resin removed, is immersed and squeezed for a few minutes. 10 g. of urea is added, and squeezing continued a few more minutes. The liquid is filtered, and the whole procedure repeated. The sample is rinsed successively with 25 ml. of 25% aq. ammonia, 50 ml. of hot water, 50 ml. of hot 5% acetic acid, and finally hot water. Loss in weight of the dry residue, less 1·5%, represents the loss of degraded cotton. J. W. B.

Comparison of Tests for Damaged Wool. H. Zahn. *Textil-Praxis*, **5**, 315–319 (May 1950).

Samples of wool were treated with acids, alkalis, reducing agents, and enzymes under prescribed conditions, and then tested for alkali solubility, dye absorption, and supercontraction in phenol and sodium bisulphite solutions, details of the tests being given. Alkali solubility was greatly increased by treatment with hydrochloric or sulphuric acid and slightly increased with phosphoric acid; the only other agent giving a marked increase in alkali solubility was sodium bisulphite. On the other hand, alkali damage had a great effect on rate of dye absorption. In phenol solution all the modified wools had a lower supercontraction than the original material, the decrease being greatest with acid damage. In sodium bisulphite solution, however, a marked decrease in supercontraction was observed only with alkali damage. A combination of these tests enables the type of damage suffered by wool to be ascertained. F. A.

Measurement and Theory of Absorbency of Cotton Fabrics. E. M. Buras, C. F. Goldthwait, and R. M. Kraemer. *Text. Research J.*, **20**, 239–248 (April 1950).

An apparatus is described which measures the rate of absorption and the ultimate absorption of water by fabrics in a simple manner, and enables a comparison of different fabrics to be made. The elimination of timing procedures and the separate evaluation of these two absorbency factors make this method unique. It can be used to study the absorption relationships of liquids and fabrics, and has many applications in the appraisal of new finishing agents. The probable mechanism of absorption is discussed. P. C.

Simple Quantitative Test for the Felting of Wool Top. H. Bogaty, D. Frishman, A. M. Sookne, and M. Harris. *Text. Research J.*, **20**, 270–276 (April 1950).

A simple and rapid method is described for measuring the felting properties of wool top. It consists in sewing lengths of wool top into cheesecloth sacks, and tumbling them for a standard time in any desired medium. The change in length of the top is regarded as a measure of felting power. The results correlate well with the shrinkage of garments made from the top, and the method thereby enables proper control of chemical treatments, e.g. shrink-resisting, to be exercised in the mill. The effects of time of tumbling, temperature, weight of sliver used, pH, and other test variables have been examined. The use of the test in research work is discussed. P. C.

Methods for the Determination of Nylon in Fibre Mixtures. J. Lanczer. *Textil-Rund.*, **5**, 92–94 (March 1950).

Nylon mixed with cellulosic fibres can be detected by diazotisation of the NH_2 groups in the nylon molecule followed by coupling in a Naphtol AS solution, a modification of the technique being used for dyed fibre mixtures. Another method depends upon the fluorescence in ultraviolet radiation of nylon treated with the Naphtol AS solution. H. K.

Measurement of Dye Strengths. E. I. Stearns. *Amer. Dyestuff Rep.*, **39**, P 358–P 366 (29th May 1950).

In a discussion on various aspects of dye strength testing, it is stated that with straight dyeings visual estimation is possible to within 5%. By using combination dyeings, e.g. dyeing a range of variable yellow concentrations while adding a constant amount of blue dye, an accuracy of 1% is attained. An account is given of strength estimation from spectrophotometric reflection data, using the Pineo formula. The three-dimensional representation of hue, value, and chroma is discussed, with the conclusion that in presence of hue variations any strength estimate is approximate. It is stressed that in all cases the exact dyeing conditions must be specified. J. W. B.

Fluorescence and the Beer–Lambert Law. A Note on the Technique of Absorption Spectrophotometry. E. A. Braude, J. S. Fawcett, and C. J. Timmons. *J.C.S.*, 1019–1021 (March 1950).

Although simple organic compounds in neutral solution are assumed to obey the Beer–Lambert law, it has been observed that the ultra-violet absorption of many substances, and particularly of those which exhibit strong fluorescence in solution, varies markedly with both concentration and cell length. The magnitude of the effects is closely dependent on the type of instrument and the experimental conditions employed, and is tentatively ascribed to the superposition of transmitted light and scattered fluorescence emission. The important bearing of these observations on the widely employed techniques of absorption spectrophotometry is discussed. Since all compounds exhibiting selective absorption in the ultraviolet may theoretically also exhibit fluorescence, deviations from the Beer–Lambert law are to be expected, but the magnitude of the effect depends on the wavelengths and intensities of the fluorescence bands. The findings are of obvious significance in relation to the use of light-absorption data for the characterisation and analysis of organic compounds, and in relation to the choice and design of instruments. The validity of the Beer–Lambert law should be tested wherever possible. H. H. H.

Comparison of Colorimetric Methods—Determination of Colour Characteristics of some Corning Filters and Fluorescent Cloths. L. R. Furlong. *Naval Research Lab. Rept.* **NRL-N-3256**, 21 pp. (9th March 1948): *Nuclear Sci. Abs.*, **3**, 232, 233 (1949): *Chem. Abs.*, **44**, 1758 (10th March 1950).

Four colour-measuring instruments—the Gaertner monochromator, the General Electric recording spectrophotometer, the Donaldson trichromatic colorimeter, and the Nutting monochromatic colorimeter—were compared by determining the colour characteristics of Corning colour filters and of four fluorescent cloths (Continental Lithograph Co.). Corning filters were used because they are widely used commercially and knowledge of their colour characteristics enables determination of an unknown colour by visual comparison with Corning filters. The fluorescent cloths were used primarily for further evaluation of the instruments. With non-luminous samples the recording spectrophotometer and the trichromatic colorimeter are equal in accuracy, speed, and convenience, but as the spectrophotometer is a non-visual instrument, the subjective error is reduced. Both of these instruments surpass

the monochromatic colorimeter in every respect except in simplicity of calculation. The Gaertner monochromator was used in preference to the recording spectrophotometer to measure the colour of luminous samples because the latter instrument cannot distinguish between reflection and fluorescence. The non-visual monochromator and the visual trichromatic colorimeter compare with each other just as do the spectrophotometer and the trichromatic colorimeter. With non-luminous substances the spectrophotometer surpasses the monochromator in speed and convenience. C. O. C.

Photoelectric Tricolorimeter. R. F. Denington. *J. Oil & Col. Chem. Assocn.*, **33**, 137–142 (March 1950).

A photoelectric tricolorimeter has been designed which is fast and easy to operate and which possesses sufficient accuracy for filing colour patterns. It uses three barrier-layer cells, each having a coloured filter (red, green, or blue) and galvanometer, so that the colour of the pattern is shown by the simultaneous deflection of the three galvanometers. Continual restandardisation of the instrument is avoided by adequate stabilisation of the light source. For the purpose of colour filing, it is preferable to characterise a colour by three figures, the first being the sum of the deflections for the red, green, and blue filters, and the other two being the percentages of the total contributed by the red and green filters respectively. It is considered that the instrument is unsuitable for patterns showing $< 5\%$ reflection in any one colour. A. S. F.

Polarising Colorimeters. S. Rösch. *Farben, Lacke, Anstrichstoffe*, **4**, 19–20 (1950): *Chem. Abs.*, **44**, 3747 (10th May 1950).

Arons' chromoscope (*Chem. Abs.*, **6**, 2867) and the colour tables calculated for it by Buchwald (*ibid.*, **35**, 2049) have been modified for use as a colorimeter. Any hue, chroma, and value can be produced. The device consists of two polarisers (one fixed), a quartz plate, a reflection polariser, a second adjustable plate, and an analyser. C. O. C.

Irradiator SV. F. I. Sadov and N. M. Vatulya. *Tekstil. Prom.*, **10**, 34 (April 1950).

A general description is given of an apparatus known as Irradiator SV, which is used for accelerated fading and photodegradation tests on textile materials. The apparatus is claimed to be far more rapid in action than any other available: thus in one instance an exposure of 300 hr. in a Fadeometer was matched by one of 5 hr. in the Irradiator. The apparatus takes samples in a form suitable for subsequent tensile testing. They are disposed on a rotating cylindrical surface, of diameter 60 cm. and length 110 cm., and face the axis. They are irradiated by a stationary bank of quartz mercury lamps, mounted inside the cylinder. The samples may be sprayed with water during exposure, if required. The apparatus is enclosed in a water-cooled jacket, and a stream of air or other gas is passed through continuously. The temperature may be maintained constant at any value in the range 4–90°C., and the R.H. at any value from 10 to 100%. A diagram of the apparatus is given. A. E. S.

Daylight Lamps. P. Rabe. *Melliand Textilber.*, **31**, 278–280 (April 1950).

A critical review of various types of daylight lamps. Entirely unsatisfactory results are given with quartz mercury lamps, as the spectral distribution and energy curves differ appreciably from those of daylight. B. K.

Fading of Coloured Materials by Light and Radiant Energy. A. H. Taylor and W. G. Pracejus. *Illum. Eng.*, **45**, (3), 149–151 (1950): *Chem. Abs.*, **44**, 3716 (25th April 1950).

Energy must be absorbed to produce a photochemical change, but absorbed radiant energy does not necessarily produce fading. 84 coloured specimens were exposed to midsummer sunlight and skylight through plate glass in Cleveland, Ohio. The glass was 0·25 in. thick and transmitted most of the ultra-violet radiation in sunlight. One portion of each specimen was covered with a Wratten 2A gelatin filter, which absorbs the ultra-violet radiation shorter than 4000A. but freely transmits energy in the visible spectrum. Results indicate that the fading of coloured textiles by daylight is principally due to radiant energy in the visible spectrum. C. O. C.

Uniformity of Grading of the American, British, and German Light-fastness Standards. I. H. Godlove. *Amer. Dyestuff Rep.*, **39**, P 215–P 221 (3rd April 1950).

The American, British, and German light-fastness standards were exposed to sunlight and in the Fade-Ometer. Fadings were measured with the G.E. (Hardy) recording spectrophotometer, and the fading was calculated from the tristimulus values obtained by integration. It was concluded that the American standards were more uniformly graded than either the German or the British standards. The method used for measuring fading is rapid and precise enough to be an economic and practical procedure for measuring fading in visual and objective terms. W. J. M.

Determination of the Fastness to Brightening of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2544. *Textil-Rund.*, **5**, 65 (Feb. 1950).

The test pattern 10 × 4 cm. is treated for 10 min. at 15–20°C. in a solution of 80% lactic acid (5 g./litre), squeezed until it contains its own weight of liquor, and dried in warm air at a maximum temp. of 60°C. H. K.

Determination of the Fastness to Mercerisation of Dyeings. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2561. *Textil-Rund.*, **5**, 99 (March 1950).

The test piece measuring 10 × 4 cm. is sewn to similar bleached unsized cotton fabric, the total weight adjusted to approx. 125 g./sq. m., and the assembly then treated for 5 min. at 15–20°C. in a 23·5% solution of caustic soda (30° Bé., sp. gr. 1·263). The test-piece is then squeezed out, washed for 5 min. in water at 70°C., and then rinsed with cold running tap-water. Souring for 5 min. in sulphuric acid (5 ml. of 66° Bé. acid per litre) is followed by washing for 10 min. in cold running tap-water and then squeezing. After cutting the stitching on three sides, the pattern is dried in warm air at a maximum temp. of 60°C. H. K.

Determination of the Fastness to Decatising of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2579. *Textil-Rund.*, **5**, 100 (March 1950).

The test patterns are laid on three layers of suitable coarse cotton fabric, covered with a similar pad, and the whole assembly laid on the perforated surface of a suitable apparatus. The pattern is decatised with saturated steam for 15 min. in either a closed or an open system. The pressure is 0·5 atm. (110°C.) for open decatising and 1·5 atm. (127°C.) for pressure decatising. The steamed pattern is hung in air, and assessed dry after 30 min. H. K.

Determination of the Fastness to Hot Pressing of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2532. *Textil-Rund.*, **5**, 64 (Feb. 1950).

DRY— The iron is placed on the test pattern (10 × 4 cm.), which is in contact with a piece of bleached cotton fabric for 10 sec. The pressure applied by the iron is to be 30 g./sq. cm., and the temp. of ironing 150°C., or 120°C. for acetate rayon.

WET— The method is similar to the above, except that the wet test pattern is laid between wet bleached untreated cotton fabric. H. K.

Determination of the Fastness to Stoving of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2574. *Textil-Rund.*, **5**, 66 (Feb. 1950).

The test pattern 10 × 4 cm. is first treated at 15–20°C. for 5 min. in an alkali-free solution (5 g./litre) of soap flakes of minimum fatty acid content 85%, squeezed until it contains its own weight of liquor, and suspended for 16 hr. on a glass hook in a 10-litre flask in which 5 g. of sulphur is burned. The sulphur is ignited in a metal dish and the flask stoppered. The pattern is hung in the air for 2 hr. before drying. Mixtures containing cellulose fibres are washed for 10 min. in cold running water before drying. H. K.

Identification of Crease-resist Finishes. H. M. Ulrich. *Textil-Praxis*, **5**, 442 (July 1950).

Methods are given for the identification of crease-resist finishes on cellulosic materials. *Phenoplastics* liberate phenol on dry distillation, which reacts with bromine to form characteristic crystals of tribromophenol. *Aminoplastics* on heating with NaOH give ammonia and methylamine, and the former is detected with Nessler's reagent. *Complex boron salts* are identified by detection of ammonia with potassium platinichloride and boron by the curcumalein reaction, giving a blue colour with an extract of curcuma root. B. K.

Use of Sleeves for Evaluating Acaricides for Clothing Treatment. H. F. Cross and R. Frye. *J. Econ. Entomol.*, **42**, 878–880 (1949): *Chem. Abs.*, **44**, 3657 (25th April 1950).

Sleeves of jackets impregnated with acaricides are used to evaluate the protection given against chigger mites. Percentage protection is calculated by 100 — number of chigger attachments to subjects wearing treated garments × 100/number of attachments to subjects wearing untreated garments. C. O. C.

Apparatus for Testing Screen-printing Lacquers and Printing Screens. K. Scholl. *Melliand Textilber.*, **31**, 125–126 (Feb. 1950).

A simple mechanically driven laboratory apparatus is described which determines within a few hours the resistance of a printing screen lacquer to both mechanical and chemical influences, thus saving considerable working time. H. K.

PATENTS

Measuring the Moisture Content of Loose Fibres and other Solid Materials. R. S. Phillips and J. Burns Ltd. *B.P.* 637,469.

When the dielectric constant of a material is measured by placing it in a receptacle between two electrodes, an error is introduced by the air between the particles of the material. This error is removed by covering the material with an inert liquid of sp. gr. < that of the material, which is non-miscible with water, and which has an adjustable dielectric constant, the range of adjustment including the dielectric constant of the material to be tested when dry. The liquid is so adjusted that when the dried material is placed in it there is no variation in the capacitance of the combination. C. O. C.

Testing Yarns subjected under Tension to Physical or Chemical Treatment. British Celanese Ltd. *B.P.* 636,567.

Each end of the sample is held and subjected to constant linear tension while being treated, there being means to record changes with time in the length of the specimen. C. O. C.

Testing the Bursting Strength of Papers and other Sheet Material. W. & R. Balston Ltd. and F. W. Balston. *B.P.* 637,306.

Apparatus for testing the bursting strength of wet or dry paper, etc. of lower strength than 1 lb./sq. in. comprises a vertical cylindrical container for the testing fluid, fitted at its lower end with an outlet, combined with a fluid-tight clamp for the test paper, and an inlet close by. Indicating means comprise two equal weights connected by a fine wire passing over one or more pulleys mounted above the container, one weight being moved by the liquid entering the container, whilst the other has an index moving over an external vertically adjustable graduated scale, the reading being zero when the inner weight is at its lowest position. An annular member helps to locate the outer weight, which can serve as a plumb bob and can be adjusted vertically on a screw-threaded stem. To carry out a test, liquid, e.g. water, is admitted to the tube, the indicating weights ceasing to move as soon as the burst occurs. For sheet material of higher strength than 1 lb. per sq. in., the weights, wire, and scale are dispensed with, and pressure gauges fitted to the vertical container, compressed air being admitted above the test fluid until bursting occurs, and the bursting pressure being indicated and recorded on the gauges. S. V. S.

XV— MISCELLANEOUS

Surface Colouring of Glass with Silver Compounds by the Diffusion Method. E. E. Mazo. *Doklady Akad. Nauk S.S.S.R.*, **68**, 745–748 (1949).

Tastes and Preferences for Colours. M. Déribéré. *Teintex*, **15**, 175–187 (April) and 215–225 (May 1950).

The extensive amount of work published in this field of taste and preference for coloured materials is reviewed and examined at length, and the psychological value of such a study is emphasised. Tables are included for males and females of all ages, showing tastes and other emotions for the various hues of the spectrum range. Generally, pure blues have first place, while red is more favoured by women than men, green is about equal, though females have a preference over males for yellow-green, whereas yellow itself and orange seem to be more favoured by men. The study is claimed to afford a useful psychological guide for human activities. H. H. H.

Stability of Colour in Fruit Juices. E. A. Nebesky, W. B. Esselen, J. E. W. McConnell, and C. R. Fellers. *Food Research*, **14**, 261–274 (1949).

PATENTS

Opaque Finish on Anodised Aluminium. W. J. Campbell and Alltones Ltd. *B.P.* 639,090.

The aluminium from the anodising bath is washed free from sulphuric acid, then immersed in aqueous ammonia, and finally after little or no rinsing treated with an oil, wax, fat, or resinous liquid. This gives an intense permanent white. The oxide film may be dyed or printed before the treatment with oil, etc., in which case a completely opaque colour results. C. O. C.

Copper-staining or Red Etching of Glass. M. M. Peterson and Corning Glass Works. *U.S.P.* 2,498,003.

Soda–lime–silicate glass is uniformly coloured deep red by first heating it in a reducing atmosphere, then applying a copper-staining composition, and again heating. C. O. C.

Flock-coated Articles having Lustrous or Glittering Surfaces. A. Selsky. *U.S.P.* 2,496,070.

The surface to be treated is coated with a tacky adhesive and then rotated rapidly while in contact with a mass of flock, so that the latter is picked up and oriented on the surface. C. O. C.

Improving the Colour of Meat. H. M. Coleman, A. H. Steffen, E. W. Hopkins, and Armour & Co. *U.S.P.* 2,491,646.

Meat and other materials containing myoglobin or hæmoglobin are coloured bright red by treating them with not < 0·3 g. of nicotinic acid per pound of meat or the like. C. O. C.